(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12422 A1

(51) International Patent Classification[7]: C11D 1/86 // 1:66, 1:72, 1:722, 1:82

(21) International Application Number: PCT/US01/20207

(22) International Filing Date: 25 June 2001 (25.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/631,757 3 August 2000 (03.08.2000) US

(71) Applicant (*for all designated States except US*): **ECOLAB INC.** [US/US]; Ecolab Center, St. Paul, MN 55102 (US).

(72) Inventors: **MAN, Victor, F.**; 1410 Carling Drive, Apt. 207, St. Paul, MN 55102 (US). **KLAERS, Karen, G.**; 6828 Benton Way, Inver Grove Heights, MN 55076 (US).

(74) Agent: **SORENSEN, Andrew, D.**; Ecolab Inc., 840 Sibley Memorial Highway, Mendota Heights, MN 55118 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/12422 A1

(54) Title: PLASTICS COMPATIBLE DETERGENT COMPOSITION AND METHOD OF CLEANING PLASTICS

(57) Abstract: A plastics compatible detergent composition is provided by the invention. The plastics compatible detergent composition includes about 0.01 wt.% to about 10 wt.% anionic surfactant; about 0.01 wt.% anionic surfactant; about 0.01 wt.% to about 10 wt.% cationic surfactant; about 0.01 wt.% to about 10 wt.% of at least one of reverse polyxyalkylene block copolymer surfactant, alcohol alkoxylate surfactant having polyoxypropylene and/or polyoxybutylene end groups, and mixtures thereof; about 0.01 wt.% to about 10 wt.% alkylpolyglycoside surfactant; and about 0.01 wt.% to about 20 wt.% silicone surfactant. A method for washing an article having a plastic surface is provided by the invention. The method includes a step of applying the detergent composition to the plastic surface, and rinsing the detergent composition from the article.

PLASTICS COMPATIBLE DETERGENT COMPOSITION AND METHOD OF CLEANING PLASTICS

Field of the Invention

The invention relates to a plastics compatible detergent composition and to a method for cleaning plastics. In particular, the plastics compatible detergent composition is a detergent composition that can be used in a conventional warewashing machine.

Background of the Invention

Many articles manufactured from plastics require periodic cleaning. Many conventional detergent compositions include chemicals that cause stress cracks in plastics. Stress cracks are the cracks that result when the plastic is exposed to chemicals (usually organic) that facilitate the release of the built-in stress (or frozen-in stress) in the plastics.

U.S. Patent No. 5,501,815 to Man discloses a plasticware-compatible low-foaming rinse aid composition. The rinse aid composition includes an alkyl polyglycoside (APG) and a reverse polyoxyethylene-containing polyoxyalkylene block copolymer.

Summary of the Invention

A plastics compatible detergent composition is provided by the invention. The plastics compatible detergent composition includes about 0.01 wt.% to about 10 wt.% anionic surfactant; about 0.01 wt.% to about 10 wt.% cationic surfactant; about 0.01 wt.% to about 10 wt.% at least one of reverse polyoxyalkylene block copolymer surfactant, alcohol alkoxylate surfactant having polyoxypropylene and/or polyoxybutylene end groups, and mixtures thereof; about 0.01 wt.% to about 10 wt.% alkylpolyglycoside surfactant; and about 0.01 wt.% to about 20 wt.% silicone surfactant.

A method for washing an article having a plastic surface is provided by the invention. The method includes a step of applying the detergent composition to the plastic surface, and rinsing the detergent composition from the article.

Detailed Description of the Invention

A plastics compatible detergent composition is provided for cleaning articles manufactured from plastics. It should be understood that the term "plastics compatible" reflects the relative compatibility of the detergent composition according to the invention with certain types of plastics compared with prior art detergent compositions that have a tendency to develop stress cracking in plastics over time. The plastics compatible detergent composition according to the invention provides reduced stress cracking when used to clean plastics compared with certain prior art detergent compositions. Types of plastics that can be cleaned with the plastics compatible detergent composition according to the invention include those polymers that have a tendency to develop stress cracking when cleaned with conventional detergents, such as, polycarbonate polymers (PC), acrilonitrile-butadiene-styrene polymers (ABS), and polysulfone polymers (PS).

Articles that can be cleaned with the plastics compatible detergent composition according to the invention are preferably articles that are manufactured from polymers that have a tendency to develop stress cracking when cleaned with conventional detergents and that generally require periodic cleaning. Exemplary articles include head protection gear, playground equipment, toys, safety windows or shields, and self-contained breathing equipment. Exemplary head protection gear includes safety helmets, sports helmets, hard hats, and safety glasses. Exemplary playground equipment includes indoor and outdoor playground equipment. In particular, certain fast food chains have polymeric indoor playground equipment that requires periodic cleaning. Exemplary safety shields include shields for helmets and masks that are used by policemen and firefighters, and in the laboratory. In addition, articles which can be cleaned include those articles having desired optical clarity including, for example, windows, bullet proof windows, safety glasses, safety shields, and underwater masks.

Types of soil that can be cleaned from articles according to the invention include those types of soils that are commonly encountered on the articles to be cleaned. Common types of soil that can be cleaned according to the invention include grease soils, carbon particulate soils, body fluid soils, and sand and/or dirt soils. An exemplary grease soil includes oil lubricant. Exemplary carbon particulate soils include soils resulting from welding and/or from fires. Exemplary body fluid soils include sweat, perspiration, and urine. It should be appreciated that a component that is intended to be present on the article surface, such as paint, is generally not considered to be soil.

The plastics compatible detergent composition according to the invention can be referred to more simply herein as the detergent composition. The detergent composition preferably includes a mixture of surfactants that tend not to cause stress cracking in plastics. The detergent composition can be used to clean articles in a conventional warewashing machine. When the detergent composition is used in a conventional warewashing machine, it is generally desirable that the detergent composition exhibits sufficiently low foaming properties so that the detergent composition can be used in a conventional warewashing machine. The detergent composition can exhibit a level of foaming which renders it unsuitable for use in a conventional warewashing machine when the detergent composition is intended to be used in an environment where foaming is not a particular concern. For example, when the detergent composition is used to wash playground equipment, it is expected that the detergent composition can exhibit a relatively high level of foaming. The detergent composition preferably includes a mixture of at least two or more of alkyl polyglycoside surfactants, reverse polyoxyalkylene copolymer surfactants, cationic surfactants, polysiloxane surfactants, and anionic surfactants.

Alkyl Polyglycoside (APG) Surfactants

The alkyl polyglycosides (APGs), also called alkyl polyglucosides if the saccharide moiety is glucose, are naturally derived, nonionic surfactants. The alkyl polyglycosides that can be used in the present invention are fatty ester

derivatives of saccharides or polysaccharides that are formed when a carbohydrate is reacted under acidic condition with a fatty alcohol through condensation polymerization. The APGs commonly are derived from corn-based carbohydrates and fatty alcohols from natural oils in animals, coconuts and palm kernels. Such methods for deriving APGs are known in the art. For example, see U.S. Patent No. 5,003,057 to McCurry. The description in U.S. Patent No. 5,003,057 relating the methods of making APGs and the chemical properties of APGs is incorporated by reference herein.

The alkyl polyglycosides that can be used in the present invention contain a hydrophilic group derived from carbohydrates and is composed of one or more anhydroglucose. Each of the glucose units can have two ether oxygens and three hydroxyl groups and a terminal hydroxyl group, imparting water solubility to the glycoside. The presence of the alkyl carbons leads to the hydrophobic activity. When carbohydrate molecules react with fatty alcohol molecules, alkyl polyglycosides molecules are formed with single or multiple anhydroglucose units, which are termed monoglycosides and polyglycosides, respectively. The final alkyl polyglycoside product typically has a distribution of varying concentration of glucose units (or degree of polymerization).

The APG that can be used in the detergent composition of the invention preferably comprises saccharide or polysaccharide groups (i.e., mono-, di-, tri-, etc. saccharides) of hexose or pentose, and a fatty aliphatic group having 6 to 20 carbon atoms. Preferred alkyl polyglycosides that can be used according to the present invention are represented by the general formula:

$$G_x\text{-O-R} \qquad \text{I}$$

wherein G is a moiety derived from reducing saccharide containing 5 or 6 carbon atoms, e.g., pentose or hexose; R is fatty aliphatic group containing 6 to 20 carbon atoms; and x is the degree of polymerization (D.P.) of the polyglycoside, representing the number of monosaccharide repeating units in the polyglycoside. Generally, x is an integer on the basis of individual molecules, but because there are statistical variations in the manufacturing process of the APG, x may be a noninteger on an average basis when referred to APG used as an ingredient for the detergent

composition of the present invention. In this invention, x preferably has a value of less than 2.5, and more preferably is within the range between 1 and 2.

Exemplary saccharides from which G can be derived are glucose, fructose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose and ribose. Because of the ready availability of glucose, glucose is preferred in the making of polyglycosides. The fatty aliphatic group, which is the substituent of the preferred polyglycoside, is preferably saturated, although unsaturated fatty group may be used.

Generally, commercially available polyglycosides have alkyl chains of C_8 to C_{16} and average degree of polymerization of 1.4 to 1.6. In this invention, specific alkyl polyglycosides will be described as illustrated in the following way: "C_{12-16} G 1.4" denotes a polyglycoside with an alkyl chain of 12 to 16 carbon atoms and an average degree of polymerization of 1.4 anhydroglucose units in the alkyl polyglycoside molecule. Commercially, alkyl polyglycoside can be provided as concentrate, aqueous solutions ranging from 50 to 70 wt-% active. Examples of commercial suppliers of alkyl polyglycosides are Henkel Corp. and Union Carbide Corp.

Table 1 shows examples of commercially available (from Henkel Corp.) alkyl polyglycosides that can be used according to the present invention. The number of carbons in the alkyl groups and the average degree of polymerization in the APGs are also shown in Table 1. The average degree of polymerization of saccharides in the APG listed varies from 1.4 to 1.7 and the chain lengths of the aliphatic groups are between

C_{8-10} and C_{12-16}.

The detergent composition of the present invention has the advantage of having less adverse impact on the environment than conventional detergent compositions. Alkyl polyglycosides used in the present invention exhibit low oral and dermal toxicity and irritation on mammalian tissues. These alkyl polyglycosides are also biodegradable in both anaerobic and aerobic conditions and they exhibit low toxicity to plants, thus improving the environmental compatibility of the rinse aid of the present invention. Because of the carbohydrate property and the excellent water

solubility characteristics, alkyl polyglycosides are compatible in high caustic and builder formulations.

TABLE 1

Examples of alkyl polyglycosides (Henkel Corp.)		
Alkyl polyglycoside	Henkel Surfactant	Ratio of APGs with Various Chain Lengths
C_{8-10} G 1.7	APG 225	C_8:C_{10} (45:55)
C_{9-11} G 1.4	APG 300	C_9:C_{10}:C_{11} (20:40:40)
C_{9-11} G 1.6	APG 325	C_9:C_{10}:C_{11} (20:40:40)
C_{12-16} G 1.4	APG 600	C_{12}:C_{14}:C_{16} (68:26:6)
C_{12-16} G 1.6	APG 625	C_{12}:C_{14}:C_{16} (68:26:6)

In Table 1, the "Ratio of APGs with Various Chain Lengths" is the ratio by weight of the amount of APG of two different alkyl chain lengths in the commercially available APG sample. For example, C_8:C_{10} (45:55) means about 45% of the APGs in the sample have alkyl chain length of 8 carbon atom and about 55% of the APGs in the sample have alkyl chain length of 10 carbon atoms. The APGs listed in Table 1 have moderate sheeting characteristics and are chemically compatible with thermoplastics such as polycarbonate and polysulfone. Because of the normal tendency of APGs to be foamy, defoamers such as long-chain ketone defoamers can be used with APGs.

The detergent composition preferably includes a sufficient amount of alkyl polyglycoside surfactant in an amount that provides a desired level of cleaning. When the detergent composition is intended to be used in a warewashing machine, the amount of alkyl polyglycoside surfactant should not be too much so that the detergent composition provides an unacceptable level of foaming so that the warewashing machine cannot adequately handle the detergent composition. Preferably, the detergent composition concentrate includes between about 0.01 wt.% and about 10 wt.% alkyl polyglycoside surfactant; more preferably between 0.1 and

3 wt.% alkyl polyglycoside surfactant; and, even more preferably, between about 0.1 and 0.6 wt.% alkyl polyglycoside surfactant.

Reverse Polyoxyalkylene Copolymer Surfactants

The reverse polyoxyalkylene copolymers, especially -$(EO)_e$-$(PO)_p$ block copolymers, are effective in reducing or minimizing the normal foaming activity or characteristic of APGs, which is quite foam-forming by itself. Unlike many defoamers, the reverse polyoxyalkylene block copolymer is capable of enhancing the sheeting characteristics of the aqueous rinse solution. It has been found that regarding chemical attack on thermoplastics, such as polycarbonate and polysulfone, the reverse polyoxyalkylene block copolymers have better thermoplastic compatibility than the normal-type polyoxyalkylene block copolymers, which have end blocks of -$(EO)_e$ in the polyoxyalkylene block copolymer chain. Because of their better water-solubility characteristics, the reverse polyoxyethylene-polyoxypropylene (i.e., reverse -$(EO)_e$-$(PO)_p$) block copolymers are preferred over other reverse polyoxyalkylene block copolymers, such as those that contain polyoxybutylene blocks.

The polyoxyalkylene block copolymers that can be used according to the present invention can be formed by reacting alkylene oxides with initiators. Preferably, the initiator is multifunctional if its use results in "multibranch" or "multiarm" block copolymers. For example, propylene glycol (bifunctional), triethanol amine (trifunctional), and ethylenediamine (tetrafunctional) can be used as initiators to initiate polymerization of ethylene oxide and propylene oxide to produce reverse block copolymers with two branches (i.e., arms or linear units of polyoxyalkylenes), three branches, and four branches, respectively. Such initiators may contain carbon, nitrogen, or other atoms to which arms or branches, such as blocks of polyoxyethylene $(EO)_e$, polyoxypropylene $(PO)_p$, polyoxybutylene $(BO)_b$, -$(EO)_e$-$(PO)_p$, -$(EO)_e$-$(BO)_b$, or -$(EO)_3$-$(PO)_p$-$(BO)_b$, can be attached. In such a copolymer, a larger amount of $(EO)_e$ results in higher water-solubility and a larger amount of $(PO)_p$ or $(BO)_b$ improves the thermoplastic compatibility of the

copolymer. The amount of $(EO)_e$, $(PO)_p$, and $(BO)_b$ in the block copolymer can be selected such that the reverse block copolymer is detersive.

The reverse block copolymer surfactants which can be used according to the invention preferably include arms or chains of polyoxyalkylenes that are attached to the residues of the initiators and contain end blocks of $-(EO)_x-(PO)_y$, which have ends of polyoxypropylene (i.e., $-(PO)_y$), wherein x is about 1 to 1000 and y is about 1 to 500, more preferably x is about 5 to 20 and y is about 5 to 20. The reverse block copolymer surfactants can be straight chain or branched.

The reverse block copolymer can have any desired number of blocks. A preferred three-block copolymer can be represented by the general formula:

$$(PO)_y-(EO)_x-(PO)_y \qquad \text{II}$$

wherein x is about 1 to 1000, preferably about 4 to 230; and y is about 1 to 500, preferably about 8 to 27. Such a copolymer can be prepared by using propylene glycol as an initiator and adding ethylene oxide and propylene oxide. The polyoxyalkylene blocks are added to both ends of the initiator to result in the block copolymers. In such a linear block copolymer, generally the central $(EO)_x$ contains the residue of the initiator and x represents the total number of EO on both sides of the initiator. Generally, the residue of the initiator is not shown in a formula such as II because it is insignificant in size and in contribution to the property of the molecule compared to the polyoxyalkylene block. Likewise, although the end block of the polyoxyalkylene block copolymer terminates in a -OH group, the end block is represented by $-(PO)_p$, $-(EO)_x$, $-(PO)_y$, and the like, without specifically showing the -OH at the end. Also, x, y, and z are statistical values representing the average number of monomer units in the blocks.

The reverse polyoxyalkylene block copolymer can have more than three blocks, an example of which is a five-block copolymer, represented by the general formula:

$$(PO)_z-(EO)_y-(PO)_x-(EO_y-(PO)_z \qquad \text{III}$$

wherein x is about 1 to 1000, preferably about 7 to 21; y is about 1 to 500, preferably about 10 to 20; and z is about 1 to 500, preferably about 5 to 20.

A chain of blocks may have an odd or even number of blocks. Also, in other embodiments, copolymers with more blocks, such as, six, seven, eight, and nine blocks, etc., may be used as long as the end polyoxyalkylene block is either $(PO)_p$ or $(BO)_b$.

As previously stated, the reverse -$(EO)_e$-$(PO)_p$ block copolymer can also have a branched structure having a trifunctional moiety T, which can be the residue of an initiator. The block copolymer is represented by the formula:

$$(PO)_z-(EO)_y-(PO)_x-T\begin{cases}(PO)_x-(EO)_y-(PO)_z\\(PO)_x-(EO)_y-(PO)_z\end{cases}\qquad \text{IV}$$

wherein x is about 0 to 500, preferably about 0 to 10; y is about 1 to 500, preferably about 5 to 12, and z is about 1 to 500, preferably about 5 to 10.

One example of trifunctional initiators that can produce such branched structures is triethanol amine, $N(CH_2CH_2OH)_3$, which results in a branched block -$(EO)_e$-$(PO)_p$ copolymer

$$(PO)_z-(EO)_y-(PO)_x-(OCH_2CH_2)-N\begin{cases}(CH_2CH_2O)-(PO)_x-(EO)_y-(PO)_z\\(CH_2CH_2O)-(PO)_x-(EO)_y-(PO)_z\end{cases}$$

wherein x is about 0 to 500, preferably about 0 to 10; and y is about 1 to 500, preferably about 5 to 12; and z is about 1 to 500, preferably about 5 to 10.

Other appropriate multifunctional initiators, for example, triols, can be carbon-based. One example of a copolymer resulting from such an initiator is represented by the formula:

$$\begin{array}{l}\quad\ CH_2-O(PO)_x-(EO)_y-(PO)_z\\ \quad\ \ |\\ H-C-O(PO)_x-(EO)_y-(PO)_z\\ \quad\ \ |\\ \quad\ CH_2-O(PO)_x-(EO)_y-(PO)_z\end{array}\qquad \text{VI}$$

wherein the value of x is about 0 to 10, y is about 5 to 12, and z is about 5 to 10.

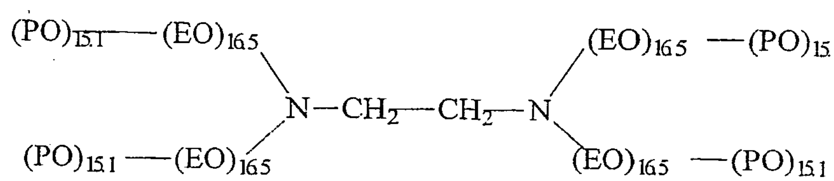
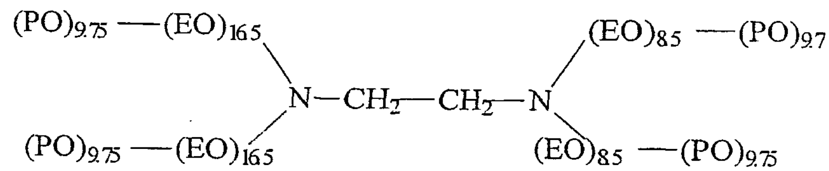
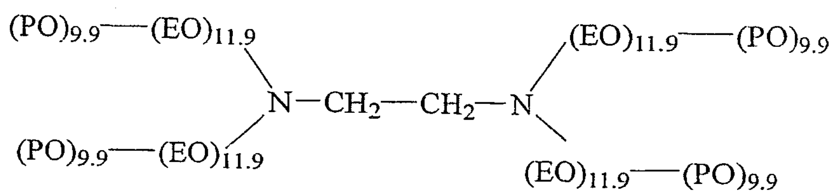
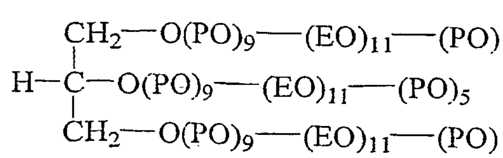
An example of a reverse block copolymer with four polyoxyalkylene arms is represented by the formula:

$$\begin{array}{ccc} (PO)_y\text{—}(EO)_x\diagdown & & \diagup(EO)_x\text{—}(PO)_y \\ & N-CH_2\text{—}CH_2\text{—}N & \\ (PO)_y\text{—}(EO)_x\diagup & & \diagdown(EO)_x\text{—}(PO)_y \end{array} \qquad \text{VI}$$

wherein x is about 1 to 500, preferably about 1 to 100; and y is about 1 to 500, preferably about 8 to 32.

The branches in multi-arm (or multi-branch) structures can each contain more than two blocks. Preferably, the end blocks are $-(PO)_p$ blocks or $-(PO)_p$-R, wherein R is a $C_{1\text{-}12}$ (lower) alkyl or a $-(BO)_b$ block with 1-5 moles of butylene oxide. Methods of making such polyoxyalkylene copolymers are known in the art and many such chemicals are commercially available (for example, TETRONIC R series from BASF Wyandotte Corporation). Table 2 shows exemplary reverse $(EO)_e$-$(PO)_p$ block. The block copolymers provided in Table 2 have an ethylene oxide content of less than about 50 wt-% of the copolymer.

Table 2

	-(EO)$_e$ -(PO)$_p$ Block Copolymers Evaluated
Designation	Structure
Polymer-1	$(PO)_{9.5}$-$(EO)_{13}$ -$(PO)_{12.5}$-$(EO)_{13}$ -$(PO)_{9.5}$
Polymer-2	$(PO)_{13}$-$(EO)_{16.5}$ -$(PO)_{12.5}$-$(EO)_{16.5}$ -$(PO)_{13}$
Polymer-3	$(PO)_{25.5}$-$(EO)_{35}$ -$(PO)_{25.5}$
TETRONIC 90R4	
TETRONIC 50R4	
GENAPOL PN30	
PLURONIC 25R2	$(PO)_{21.6}$-$(EO)_{14.2}$-$(PO)_{21.6}$
PLURONIC L10	$(PO)_{10}$-$(EO)_{11}$-$(PO)_{16}$-$(EO)_{11}$-$(PO)_{10}$
Polymer-9	C_4H_9-$(PO)_{5.3}$-$(EO)_{10.7}$-$(PO)_{20.7}$-$(EO)_{10.7}$-$(PO)_{5.3}$-C_4H_9
Polymer-10	
Polymer-11	$(PO)_{11}$-$(EO)_{11}$-$(PO)_{7}$-$(EO)_{11}$-$(PO)_{11}$

TETRONIC 90R4, TETRONIC 50R4, PLURONIC 25R2, and PLURONIC L10 can be obtained from BASF Wyandotte Corporation. GENAPOL PN30 can be obtained from Hoechst Celanese Corporation.

Although examples of reverse $(EO)_e$-$(PO)_p$ block copolymer (i.e., -$(EO)_e$-$(PO)_p$ block copolymers) are specifically described, other polyoxyalkylene block copolymers, such as -$(EO)_e$-$(BO)_b$ and $(EO)_e$-$(PO)_p$-$(BO)_b$ block copolymers, and the like, can be applied in a similar manner as the -$(EO)_e$-$(PO)_p$ block copolymers. In such cases, the $(BO)_p$ blocks can take the place of some of the $(PO)_p$ blocks in the -$(EO)_e$-$(PO)_p$ block copolymers. It is understood that one skilled in the art can modify an organic compound with $(EO)_e$, $(PO)_p$, and $(BO)_b$ moieties in a way to obtain substances not specifically disclosed in the embodiments of the present invention to accomplish essentially the same function in the same way as the invention to attain low-foaming and compatibility with thermoplastics such as polycarbonate and polysulfone.

The detergent composition preferably includes an amount of reverse polyoxyalkylene copolymer surfactant that provides a desired level of cleaning. In general, too much reverse polyoxyalkylene copolymer surfactant increases cost. Preferably, the amount of reverse polyoxyalkylene copolymer surfactant provided in the detergent composition concentrate is between about 0.01 wt.% and about 10 wt.%, and more preferably between 0.1 wt.% and 5 wt.%, and, even more preferably, between 0.5 wt.% and 1 wt.%.

Another surfactant that can be used in place of the reverse polyoxyalkylene copolymer surfactant or in combination with the reverse polyoxyalkylene copolymer surfactant is an alcohol alkoxylate surfactant with polyoxypropylene $(PO)_x$ and/or polyoxybutylene $(BO)_y$ end groups or end blocks wherein x is about 1 to 1000 and y is about 1 to 500. The alcohol alkoxylate surfactant with polyoxypropylene and/or polyoxypropylene end group can be referred to as a polyoxyalkylene alcohol alkoxylate surfactant. The alcohol alkoxylate surfactant can be provided in the amount identified above.

Cationic Surfactants

The cationic surfactants that can be used in the detergent composition include alkoxylated cationic ammonium surfactants. Preferred alkoxylated cationic ammonium surfactants have the following general formula:

$$R_3 - \overset{\displaystyle R_1}{\underset{\displaystyle X}{\overset{|}{\underset{|}{N}}}} - R_2 \quad A^- \qquad \text{VIII}$$

wherein A^- represents a counter anion such as chloride, acetate, or phosphate, R_1, R_2, R_3, independently of each other, represent alkyl groups each containing 1-4 carbon atoms, and X represents $-(PO)_m$ or $-(PO)_m\,(EO)_n$ or $-(EO)_n\,(PO)_m$, wherein m is a number that ranges from about 1 to about 100, preferably 5 to 50, and n is a number that ranges from about 0 to about 50, preferably 5 to 50, and m + n is preferably from about 1 to about 100, and more preferably 5 to 50. Preferably, A^- is acetate, R_1 is a methyl group, R_2 and R_3 are ethyl groups, and X is a polyoxypropylene group having between 5 and 50 repeating units.

The detergent composition preferably includes an amount of the cationic surfactant that provides a desired level of detergency. Too much cationic surfactant tends to increase the cost of the detergent composition. Preferably, the detergent composition concentrate according to the invention includes a cationic surfactant in an amount of between about 0.01 wt.% and about 10 wt.%, preferably between 0.1 wt.% and 3 wt.%, and, more preferably, between 0.3 wt.% and 0.8 wt.%.

Silicone Surfactants

The silicone surfactant that can be used in the detergent composition according to the invention preferably includes a polysiloxane hydrophobic group modified with one or more pendant hydrophilic polyalkylene oxide groups. Such silicone surfactants provide a detergent use composition having low surface tension, high wetting, antifoaming and stain removal. The silicone surfactant can be advantageously used in a detergent composition with the first surfactant for reducing

the surface tension of the aqueous solutions, or use solution, to less than about 35 dynes/cm, and preferably between about 35 and about 15 dynes/cm, and more preferably between about 30 and about 15 dynes/cm. It should be appreciated that the detergent composition use solution has a measurable surface tension. In general, this means that the surface does not hydrophobicize to an extent that would provide an inaccurate or unmeasurable surface tension value. Preferably, the surface tension can be measured using the Wilhemy plate method. The silicone surfactants that can be used according to the invention are preferably nonionic or ionic (i.e., amphoteric).

Preferred silicone surfactants that can be used according to the invention can be characterized as polydialkyl siloxanes, preferably polydimethyl siloxanes to which hydrophilic group(s), such as polyethylene oxide, have been grafted through a hydrosilation reaction. The process results in an alkyl pendent (AP type) copolymer, in which the hydrophilic groups are attached along the siloxane backbone through a series of hydrolytically stable Si-C bond. The modified polydialkyl siloxane surfactants can have the following generic formulae:

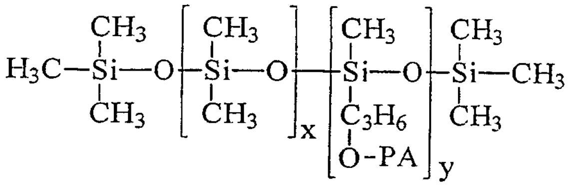
$$R_3Si\text{-}O\text{-}(R_2SiO)_x(\underset{\displaystyle PE}{\underset{|}{R_2SiO}})_y\text{-}SiR_3 \qquad \text{IX}$$

$$\underset{\displaystyle R_2\text{-}Si}{\overset{\displaystyle PE}{|}}\text{-}O\text{-}(R_2SiO)_x\text{-}\underset{\displaystyle Si\text{-}R_2}{\overset{\displaystyle PE}{|}} \qquad \text{X}$$

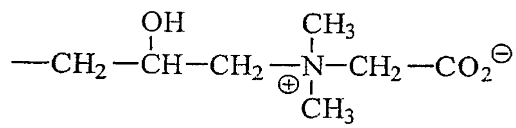
wherein PE represents a nonionic group, preferably $-CH_2-(CH_2)_p-O-(EO)_m(PO)_n-Z$, EO representing ethylene oxide, PO representing propylene oxide, x is a number that ranges from about 0 to about 100, y is a number that ranges from about 1 to 100, m, n and p are numbers that range from about 0 to about 50, $m+n \geq 1$ and Z represents hydrogen or R wherein each R independently represents a lower (C_{1-6}) straight or branched alkyl. Preferably, p is a number from 0 to 6, and R is methyl.

Preferred silicone surfactants have the formula:

XI



PA = $—(C_2H_4O)_a(C_3H_6O)_bR$ or



wherein x represent a number that ranges from about 0 to about 100, y represent a number that ranges from about 1 to about 100, a and b represent numbers that independently range from about 0 to about 60, a+b ≥ 1, and each R is independently H or a lower straight or branched (C_{1-6}) alkyl. A preferred silicone surfactant having formula XI includes x + y of about 24 to about 30, y of about 4 to about 7, the ratio of a/b being about 0.25, R being H, PA having a molecular weight of between about 800 and about 950, and the silicone surfactant having a molecular weight of between about 5,500 and about 6,500. A preferred silicone surfactant satisfying this criteria is available under the name ABIL® B 8852. A preferred silicone betaine surfactant is provided where x + y is about 16 to about 21, y is about 4 to about 7, and the molecular weight of the silicone betaine surfactant is between about 2,000 and 3,000. A silicone surfactant generally satisfying this criteria is available under the name ABIL® B 9950. Preferred silicone surfactants according to Formula XI include at least one of the following: y is less than 9, more preferably between 2 and 8; x is 0 to 90, more preferably 1 to 90; a is 1 to 60, more preferably 1 to 40, and, alternatively, 1 to 15 or 20 to 30; and b is 1 to 60, more preferably, 1 to 40, and, alternatively, 1 to 14 or 20 to 30.

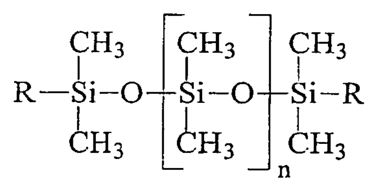
Preferred silicone surfactants are sold under the SILWET® trademark or under the ABIL® B trademark. One preferred silicone surfactant, SILWET® L77, has the formula:

$$(CH_3)_3Si\text{-}O(CH_3)Si(R^1)O\text{-}Si(CH_3)_3 \qquad \text{XII}$$

wherein R^1 is $-CH_2CH_2CH_2\text{-}O\text{-}(CH_2CH_2O)_zCH_3$ and wherein z is 4 to 16 preferably 4 to 12, most preferably 7-9.

Another class of silicone surfactants is an end-blocked (AEB type). Preferred AEB type silicone surfactants have the following general formula:

XIII



$$R = -(CH_2)_3\text{-}O\text{-}(C_2H_4O)_x(C_3H_6O)_y\text{-}$$

wherein x represents 0 to 100, y represents 1 to 100, x + y represent 1 to 200.

The detergent composition includes an amount of silicone surfactant to provide a desired level of detergency. If the detergent composition is to be used in a warewashing machine, it is desirable to provide a sufficient amount silicone surfactant to reduce foaming when foaming is undesirable. If the composition is not to be used in a warewashing machine and foaming is not a particular concern, the maximum amount of silicone surfactant provided in the detergent composition is generally a function of cost. The detergent composition concentrate preferably includes an amount of silicone surfactant that is between about 0.01 wt.% and about 20 wt.%, preferably between 0.1 wt.% and 10 wt.%, and, more preferably, between 0.5 wt.% and 3 wt.%.

Anionic Surfactants

The anionic surfactants that can be used in the detergent composition include those surfactants that disperse particulates and provide desired cleaning properties. Preferred anionic surfactants are those that tend not to form insoluble complexes with calcium and magnesium. It should be appreciated that anionic

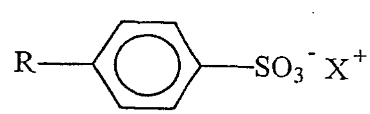
surfactants that do form insoluble complexes with calcium and magnesium can be used in the detergent composition, but when such anionic surfactants are used it is generally desirable to provide a chelating agent to handle calcium and magnesium that may be present. The incorporation of a chelating agent tends to increase the expense of the detergent composition and detracts from the amount of other surfactant components that can be incorporated into the detergent composition. In addition, the anionic surfactant is preferably one that does not generate too much foaming if the detergent composition is intended to be used in a warewashing machine.

Preferred anionic surfactants that can be used according to the invention include sulfates, sulfonates, and carboxylates.

Preferred sulfate surfactants include alkyl sulfates and alkylether sulfates wherein the alkyl group includes between about 6 and 18 carbon atoms, and more preferably between about 12 and 14 carbon atoms. Particularly preferred sulfates include lauryl sulfate and laurylether sulfate.

Sulfonate surfactants that can be used in the detergent composition include monosulfonates and disulfonates. Particularly preferred sulfonates include alkyl benzene sulfonates, alkyl sulfonates, alkyl diphenylene oxide disulfonates, and alphaolefin sulfonates, wherein the alkyl group contains between about 6 and 18 carbon atoms, and more preferably between about 12 and 14 carbon atoms.

Preferred alkyl benzene sulfonate surfactants have the following formula:



XIV

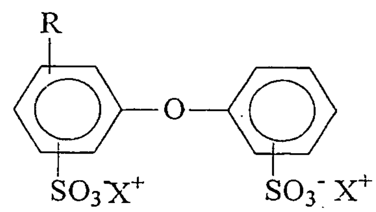
wherein R is an alkyl group having 6 to 18 carbon atoms (preferably 12 to 14 carbon atoms) and X^+ is a counter ion. Preferred counter ions include sodium, potassium, and magnesium. The alkyl benzene sulfonates can be linear or branched. Linear alkyl benzene sulfonates are preferred because they are more biodegradable than the branched alkyl benzene sulfonates.

Preferred alkyl sulfonates have the following formula:

$$R—SO_3^- X^+ \qquad XV$$

wherein R is an alkyl group having 6 to 18 carbon atoms (preferably 12 to 14 carbon atoms) and X is a counter ion. Preferred counter ions include sodium, potassium, and magnesium. The alkyl group can be linear or branched.

Preferred alkyl diphenylene oxide disulfonate have the following formula:



XV

wherein R is an alkyl group having 4 to 18 carbon atoms (preferably 6 to 12 carbon atoms) and X^+ is a counter ion. Preferred counter ions include sodium, potassium, and magnesium. The alkyl group can be linear or branched. An alkyl diphenylene oxide disulfonate having an alkyl group with 6 carbon atoms is available under the name Dowfax Hydrotope from Dow Chemical.

Alphaolefin sulfonates have the following formula:

$$CH_3(CH_2)_n - CH = CH\text{-}CH_2\text{-}SO_3^- X^+ \qquad XVII$$

wherein n is 6 to 20 and X^+ is a counter ion and is preferably sodium, potassium, or magnesium.

Carboxylates that can be used according to the invention include alcohol ethoxy carboxylates having the formula:

$$R—(EO)_x—\overset{\overset{\displaystyle O}{\|}}{C}—O^- X^+ \qquad XVII$$

wherein R is an alkyl or alkyl benzene group having 8 to 18 carbon atoms, x is a number ranging from 1 to 20 and preferably 2 to 10, and X^+ is a counter ion and is preferably sodium, potassium, or magnesium.

The detergent composition preferably includes an amount of the anionic surfactant that provides a desired level of detergency. If the detergent composition is to be used in a warewashing machine, it is desirable to limit the

amount of anionic surfactant to an amount that does not result in an undesirable amount of foaming. If the detergent composition is not to be used in a warewashing machine, the maximum amount of anionic surfactant can be determined by cost. Preferably, the detergent composition concentrate according to the invention includes a anionic surfactant in an amount of between about 0.01 wt.% and about 10 wt.%, preferably between 0.1 wt.% and 3 wt.%, and, more preferably, between 0.3 wt.% and 0.8 wt.%.

In a preferred detergent composition according to the invention, the weight ratio of combined reverse polyoxyalkylene copolymer surfactant and silicone surfactant to combined alkyl polyglycoside surfactant and anionic surfactant is between about 5:1 and about 1:1.

Additional Components

Optional ingredients can be included to facilitate the east of utilization of the detergent composition. For example, "KATHON CG/ICP" is a preservative effective for preserving APGs against microbial attack; "SAP GREEN" is a green dye; and SXS, DOWFAX 3B2, PETRO 22, NAS-8D, PETRO AA, and PETRO LBA are all commercially available anionic hydrotropes. Such anionic hydrotropes are useful for maintaining product stability and preventing phase separation over time. These anionic hydrotropes have been found to be "neutral" to plastics in that they do not protect or damage plastics. When the formulated detergent compositions are diluted to the concentration typically used for rinsing ware, the optional ingredients are diluted to such a low concentration that they no longer perform any significant function.

Chelating agents can be incorporated into the detergent composition according to the invention, when desired. Chelating agents that can be used according to the invention are those that are conventionally used in the detergent industry. Exemplary chelating agents include amino carboxylates. Exemplary amino carboxylates include nitrilo-triacetic acid (NTA), ethylene diamine, tetra-acetic acid (EDTA), and diethylene triamine penta-acetic acid (DTPA). In addition, builders that can be used according to the invention are those builders that are

conventional in the detergent industry. It should be appreciated that chelating agents and builders are desirable to protect the anionic surfactant. Accordingly, the amount of anionic surfactant is preferably provided so that the weight ratio of anionic surfactant to builder is between about 1:5 and about 5:1 and preferably about 1:1 based upon the anionic surfactant and the builder having the same active level.

The detergent composition can be applied to an article as a concentrate or it can be further diluted with water. Preferably, the detergent composition is applied to the article surface that is a plastics material in need of cleaning to provide a soak time or residence time that allows the detergent composition to interact with the soil provided on the surface of the article. Preferably, the soak time or residence time is sufficient to allow the detergent composition to provide a desired level of cleaning. In addition, the detergent composition should be sufficiently active so that the cleaning time is not too long. Preferably, the soak time or residence time is at least about 10 seconds, and more preferably between about one minute and about ten minutes, and, more preferably, between about one minute and about five minutes. In the case of relatively large articles such as playground equipment, the detergent composition can be rinsed from the article. In the case of smaller articles such as helmets, the article can be placed in a warewashing machine and washed during a conventional wash cycle. A preferred rinse agent for rinsing the article is water. The detergent composition is preferably applied to an article by spraying onto the article surface. The articles can then be rinsed or placed in a warewashing machine for further washing and/or rinsing. Furthermore, the articles can be cleaned by placing the articles in a warewashing machine and washing by applying the detergent composition in the warewashing machine. When the detergent composition is applied in a warewashing machine, it is expected that the use solution will be more dilute.

During the cleaning of the article surface, it is preferable that the article is not too hot or exposed to a use solution that is too hot. Preferably, the detergent composition used to clean the article surface is provided at a temperature of between about 50° F and about 170° F, more preferably between 85° F and 140° F, and even more preferably between 100° F and 120° F. In addition, it is preferred

that the rinse solution is provided within these temperature ranges. It is expected that if the temperature of the use solution or the rinse solution is too hot, it may cause stress cracking in the article.

Preferred techniques for cleaning an article surface include at least one of the following: (a) applying the detergent composition to the article and then either rinsing the detergent composition from the article outside of a warewashing machine or rinsing the detergent composition from the article utilizing a wash and/or rinse cycle in a warewashing machine, and with or without the addition of further detergent composition inside the warewashing machine; and (b) placing an article within a warewashing machine and applying detergent composition to the article within the warewashing machine and rinsing the article within the warewashing machine.

It is preferable that the detergent composition is relatively plastic safe. That is, an article can be washed multiple times without developing observable stress cracking. Preferably, the article can be washed at least ten times, and even more preferably at least 25 times, without developing observable stress cracking. In contrast, it is expected that caustic based cleaning solutions having a pH of 12 or higher will have a greater tendency to cause stress cracking in articles manufactured from polycarbonate polymers, acrilonitrile-butadiene-styrene polymers, and polysulfone polymers. The detergent composition according to the invention preferably provides a use solution having a pH of between about 5 and about 8.

When the detergent composition is applied directly to the plastics material to be cleaned, the detergent composition preferably has a viscosity which allows it to be applied to the plastics material via spray application, and which will then stay in contact with the plastics material. Preferably, the viscosity of the detergent composition is between about 200 and about 800 centipoise, more preferably between about 250 and 700 centipoise, and even more preferably between 300 and 600 centipoise. The viscosity can be measured using a Brookfield viscometer having a number 2 spindle and operated at 0.5 rpm.

The detergent composition that can be applied to plastics material by spray application preferably has the weight percent of components identified in

Table 3. It should be understood that the weight percent of each component is expressed based upon 100% active for each active component. Components having an active level of less than 100% can be used although the amount expressed in Table 2 is based upon a 100% active level.

Table 3

Component	Range (wt.%)	Preferred Range (wt.%)	More Preferred Range (wt.%)
anionic surfactant	0.01-10	0.1-3	0.3-0.8
cationic surfactant	0.01-10	0.1-3	0.3-0.8
reverse polyoxyalkylene copolymer surfactant	0.01-10	0.1-5	0.5-1
alkyl polyglycoside surfactant	0.01-10	0.1-3	0.1-0.6
silicone surfactant	0.01-20	0.1-10	0.5-3
builder/chelating agent/ sequestrant	0-10	0.5-6	1-4
other (water, thickener, dye, fragrance)	balance	balance	balance

The concentration identified in Table 3 can be further diluted or not further diluted to provide a use solution that is applied to the article surface. A preferred diluent includes water. For a use solution applied directly to an article surface outside of a warewashing machine environment, it is expected that the use solution will have an active concentration of between about 2 wt.% and about 10 wt.%, and, more preferably, between about 6 wt.% and about 9 wt.%. In addition, it is expected that the active concentration of the use solution used in a warewashing machine will be between about 0.005 wt.% and about 3 wt.%, and, more preferably, between about 0.02 wt.% and about 1 wt.%. It should be understood that the active concentration refers to the concentration of surfactants, builder, chelating agents, and sequestrants provided in the use solution. The active concentration generally excludes water, thickeners, dyes, and fragrances. In addition, it should be understood that when the detergent composition is applied to an article surface in a

warewashing machine, it is expected that a relatively high concentrate of the detergent composition will be fed to the warewashing machine, and that the warewashing machine will dilute the detergent composition with water to provide the use solution that is applied to the article surface.

A preferred detergent composition is provided in Table 4 where the active level of each component is 100% unless specifically indicated to the contrary.

Table 4

Percent	Raw Material
91.675	Water, Zeolite softened
0.840	EP PO Polymer; D-097
0.280	Lauryl Polyglucose 50%
0.400	Dowfax C6L
1.000	Polyether Siloxane; Abil B 8852
0.500	Linear Dodecyl Benzene Sulfonic Acid 97%
2.000	Tetrasodium EDTA Liq. 40%
0.500	Propoxylated Quaternary Ammonium Chloride
2.500	Acusol 820 Thickener
0.300	Potassium Hydroxide, 45% Liquid
0.005	Sandolan Blue E-HRL 100%, Acid Blue 182

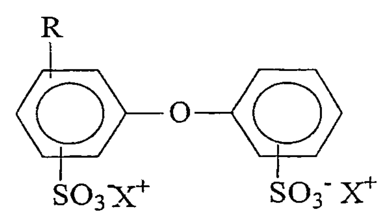
The above specification provides a complete description of the manufacture and use of the composition of the invention. Since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended.

WE CLAIM:

1. A plastics compatible detergent composition comprising:
   (a) about 0.01 wt.% to about 10 wt.% anionic surfactant;
   (b) about 0.01 wt.% to about 10 wt.% cationic surfactant;
   (c) about 0.01 wt.% to about 10 wt.% at least one of reverse polyoxyalkylene block copolymer surfactant, alcohol alkoxylate surfactant having polyoxypropylene and/or polyoxybutylene end groups, and mixtures thereof;
   (d) about 0.01 wt.% to about 10 wt.% alkyl polyglycoside surfactant; and
   (e) about 0.01 wt.% to about 20 wt.% silicone surfactant.

2. A plastics compatible detergent composition according to claim 1, wherein the anionic surfactant comprises at least one of sulfate, sulfonates, and carboxylate.

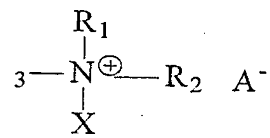
3. A plastics compatible detergent composition according to claim 1, wherein the anionic surfactant comprises alkyl diphenylene oxide disulfonate having the formula:



wherein R is an alkyl group having 6 to 18 carbon atoms and X^+ is counter ion.

4. A plastics compatible detergent composition according to claim 1, wherein the anionic surfactant comprises at least one of lauryl sulfate and lauryl ether sulfate.

5. A plastics compatible detergent composition according to claim 1, wherein the cationic surfactant comprises an alkoxylated cationic ammonium surfactant having the formula:



wherein A^- represents a counter anion, R_1, R_2, and R_3, independently of each other, are alkyl groups of 1-4 carbon atoms, and X is $-(PO)_m$ or $-(PO)_m(EO)_n$ or $-(EO)_n(PO)_m$ wherein m is about 1 to about 100 and n is about 0 to about 50.

6. A plastics compatible detergent composition according to claim 5, wherein the counter anion is at least one of chloride, acetate, and phosphate.

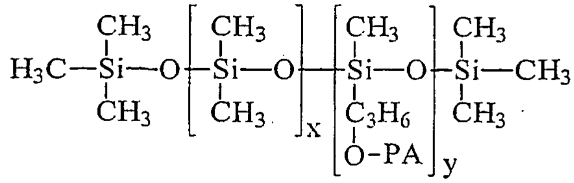
7. A plastics compatible detergent composition according to claim 1, wherein the reverse polyoxyalkylene block copolymer surfactant comprises a polyoxyethylene-polyoxypropylene block copolymer.

8. A plastics compatible detergent composition according to claim 1, wherein the alkyl polyglycoside surfactant comprises a surfactant having the formula:

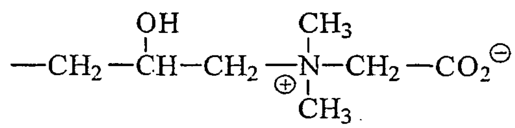
$$G_x\text{-O-R}$$

wherein G is moiety drive from reducing saccharide containing 5 or 6 carbon atoms, R is a fatty aliphatic group containing 6 to 20 carbon atoms, and x is less than 2.5.

9. A plastics compatible detergent composition according to claim 1, wherein the silicone surfactant has the following formula:



PA = $—(C_2H_4O)_a(C_3H_6O)_bR$ or

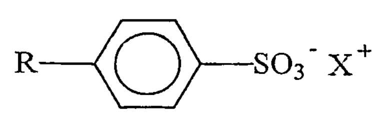


wherein x is a number ranging from 0 to 100, y is a number from 1 to 100, a and b are numbers that independently are 0 to 60 with the proviso that a + b is greater than or equal to 1, and each R is independently H or lower straight or branched C_{1-6} alkyl group.

10. A plastics compatible detergent composition according to claim 1, wherein the anionic surfactant comprises a sulfate surfactant having an alkyl group containing between 6 and 18 carbon atoms.

11. A plastics compatible detergent composition according to claim 10, wherein the sulfate surfactant comprises at least one of lauryl sulfate and lauryl ether sulfate.

12. A plastics compatible detergent composition according to claim 1, wherein the anionic surfactant comprises an alkyl benzene sulfonate surfactant having the formula:



wherein R is an alkyl group having 6 to 18 carbon atoms and X^+ is a counter ion.

13. A plastics compatible detergent composition according to claim 1, wherein the anionic surfactant comprises an alkyl sulfonate having the formula:

$$R—SO_3^-\ X^+$$

wherein R is an alkyl group having 6 to 18 carbon atoms and X^+ is a counter ion.

14. A plastics compatible detergent composition according to claim 1, wherein the anionic surfactant comprises a carboxylate having the formula:

$$R\text{—}(EO)_x\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O^-\ X^+$$

wherein R is an alkyl or alkyl benzene group having 8 to 18 carbon atoms, x is a number ranging from 1 to 20, and X^+ is a counter ion.

15. A method for washing an article having a plastic surface, the method comprising steps of:

(a) applying a detergent composition to the plastic surface, the detergent composition comprising:

(i) about 0.01 wt.% to about 10 wt.% anionic surfactant;

(ii) about 0.01 wt.% to about 10 wt.% cationic surfactant;

(iii) about 0.01 wt.% to about 10 wt.% at least one of reverse polyoxyalkylene block copolymer surfactant, alcohol alkoxylate surfactant having polyoxypropylene and/or polyoxybutylene, and mixtures thereof;

(iv) about 0.01 wt.% to about 10 wt.% alkyl polyglycoside surfactant; and

(v) about 0.01 wt.% to about 20 wt.% silicone surfactant; and

(b) rinsing the detergent composition from the article.

16. A method according to claim 15, wherein the plastic surface comprises at least one of polycarbonates polymers, acrilonitrile-butadiene-styrene polymers, and polysulfone polymers.

17. A method according to claim 15, wherein the step of applying comprises providing the detergent composition with a residence time on the plastic surface of between about 10 seconds and about 10 minutes.

18. A method according to claim 15, further comprising a step of:
    (a) rinsing the article in a warewashing machine.

19. A method according to claim 15, wherein the detergent composition has a viscosity between about 200 cps and about 800 cps measured using a Brookfield viscometer having a number 2 spindle and operated at 5 rpm.

20. A method according to claim 15, wherein the detergent composition has an active concentration of between about 2 wt.% and about 10 wt.%.

21. A method according to claim 15, wherein the step of applying a detergent composition to the plastic surface further comprises diluting the detergent composition to provide a use solution having an active concentration of between about 0.005 and about 3 wt.%.

22. A method according to claim 21, wherein the use solution is applied to the plastic surface inside a warewashing machine.

23. A method according to claim 15, wherein the detergent composition has a pH of between about 5 and about 8.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/20207

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D1/86 //C11D1:66,C11D1:72,C11D1:722,C11D1:82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 501 815 A (MAN VICTOR F) 26 March 1996 (1996-03-26) cited in the application claims 1,20; table 3	1,7,8, 15-23
X	EP 0 875 556 A (ECOLAB INC) 4 November 1998 (1998-11-04) claims 1,4,7,16; example I3	1,2,7,9, 15-23
X	WO 00 31224 A (HENKEL KGAA) 2 June 2000 (2000-06-02) claim 1; table 1	1,2,4,8, 10,11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 January 2002	28/01/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Saunders, T

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 01/20207

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5501815	A	26-03-1996	AU	685949	B2	29-01-1998
			AU	2516595	A	19-04-1996
			CA	2197095	A1	04-04-1996
			CN	1174568	A ,B	25-02-1998
			DE	69503144	D1	30-07-1998
			DE	69503144	T2	05-11-1998
			DK	783559	T3	16-11-1998
			EP	0783559	A1	16-07-1997
			JP	10506146	T	16-06-1998
			NZ	285683	A	28-07-1998
			WO	9610068	A1	04-04-1996
EP 0875556	A	04-11-1998	US	5880088	A	09-03-1999
			US	5880089	A	09-03-1999
			AU	5641698	A	05-11-1998
			BR	9801056	A	14-12-1999
			EP	0875556	A2	04-11-1998
			JP	10310799	A	24-11-1998
WO 0031224	A	02-06-2000	DE	19853720	A1	25-05-2000
			WO	0031224	A1	02-06-2000
			EP	1133545	A1	19-09-2001

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : **B08B 3/04, 3/12**	A1	(11) International Publication Number: **WO 97/34711** (43) International Publication Date: 25 September 1997 (25.09.97)

(21) International Application Number: PCT/US97/00016

(22) International Filing Date: 15 January 1997 (15.01.97)

(30) Priority Data:
08/617,606 19 March 1996 (19.03.96) US

(71) Applicant: CHURCH & DWIGHT COMPANY, INC. [US/US]; 469 North Harrison Street, Princeton, NJ 08543 (US).

(72) Inventors: CALA, Francis, R.; 308 South Second Avenue, Highland Park, NJ 08904 (US). REYNOLDS, Richard, A.; 10-P Dennis Drive, Hightstown, NJ 08500 (US).

(74) Agents: DEPAOLI, George, A.; Suite 1103, 2231 Crystal Drive, Arlington, VA 22202 (US) et al.

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: AQUEOUS ALKALI CLEANING COMPOSITIONS

(57) **Abstract**

Aqueous alkali cleaning compositions containing an alkali metal salt, an N-alkyl pyrrolidone derivative, and specific ethylene oxide/propylene oxide block copolymers having molecular weights of from about 1500 to about 2500. Such compositions can be employed as an aqueous concentrate or solution to clean a substrate such as a circuit board, wiring board or metal surface. Specific ethylene oxide/propylene oxide block copolymers protect plastic parts from corrosion by N-alkyl pyrrolidone derivatives without compromising N-alkyl pyrrolidone derivative cleaning ability.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

AQUEOUS ALKALI CLEANING COMPOSITIONS

BACKGROUND OF THE INVENTION

The present invention is directed to improvements in aqueous alkali cleaning compositions. In particular, the present invention is concerned with aqueous alkali cleaning compositions which contain an N-alkyl pyrrolidone derivative and a specific compound for preventing corrosion of plastic.

It has been found that solder fluxes contained on electronic circuit assemblies, such as printed circuit boards and printed wiring boards, can be effectively removed by contact with aqueous compositions of alkaline salts such as alkali metal carbonates and alkali metal bicarbonates and mixtures thereof. Addition of certain surfactants, especially N-alkyl pyrrolidone derivatives, to aqueous compositions of alkaline salts improves cleaning effectiveness of aqueous alkaline solutions. N-alkyl pyrrolidone derivatives which are particularly good cleaning surfactants are the N-(n-C_6-C_{14}) 2 pyrrolidones. Such pyrrolidones have been employed in aqueous alkaline compositions to clean printed circuit boards and wiring boards of solder fluxes and other contaminants, and to clean contaminants from metal surfaces. It has further been found that addition of certain compounds such as alkali metal silicates, magnesium salts and the like to such formulations greatly improves corrosion protection of ceramic and metal components on such electronic assemblies.

Cleanliness of electronic circuit assemblies (ECA), such as printed circuit boards (PCB) or printed wiring boards (PWB), is regarded as being critical to their functional reliability. Ionic and nonionic contamination on circuit assemblies is believed to contribute to premature failures of circuit assemblies by allowing short circuits to develop.

In the manufacture of electronic circuit assemblies, ionic and nonionic contamination can accumulate after one or more steps of the process. Circuit assembly materials are plated, etched, handled by operators in assembly, coated with corrosive or potentially corrosive fluxes and finally soldered.

In fabrication of electronic circuit assemblies, e.g., printed circuit boards, soldering fluxes first are applied to a substrate board material to ensure firm, uniform bonding of the solder. These soldering fluxes fall into two broad categories: rosin and non-rosin, or water soluble, fluxes. Rosin fluxes, which are moderately corrosive and have a much longer history of use, still are used widely throughout the electronics industry. Water soluble fluxes, which are a more recent development, are being used increasingly in consumer products applications. Because water soluble fluxes contain strong acids and/or amine hydrohalides, such fluxes are very corrosive. Unfortunately, residues of any flux can cause circuit failure if residual traces of flux are

not removed carefully following soldering and thus remain on an electronic circuit assembly.

While water soluble fluxes can be removed with warm, soapy water, removal of rosin flux from printed circuit boards is more difficult and has therefore traditionally been carried out with the use of chlorinated hydrocarbon solvents such as 1,1,1,-trichlorethane, trichloroethylene, trichloromonofluoromethane, methylene chloride, trichlorotrifluoroethane (CFC113), tetrachlorodifluoroethane (CFC112) or mixtures or azeotropes of these and/or other solvents. Such solvents are undesirable, however, because they are toxic, and when released into the environment deplete the ozone layer and/or contribute to the greenhouse global warming effect and are not readily biodegradable and thus are hazardous for long periods of time. Thus, use of such solvents is subject to close scrutiny by the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA), and stringent containment equipment must be used.

Alkaline cleaning compounds known as alkanolamines, usually in the form of monoethanolamine, have been used for rosin flux removal as an alternative to toxic chlorinated hydrocarbon solvents. Such high pH compounds (e.g., about 12 pH), chemically react with rosin flux to form a rosin soap through the process of saponification. Other organic substances such as surfactant or alcohol derivatives can be added to alkanolamine cleaning compounds to facilitate removal of such rosin soap. Unfortunately, such

organic compounds, as well as water soluble soldering fluxes, have a tendency to cause corrosion on surfaces and interfaces of printed wiring boards if such compounds and fluxes are not completely and rapidly removed during fabrication of wiring and circuit boards.

In other approaches, Daley et al., U.S. Patent No. 4,635,666 utilize a highly caustic solution having a pH of 13 in a batch cleaning process. This method severely oxidizes solder applied to circuit boards. In Hayes et al., U.S. Patent Nos. 4,640,719 and 4,740,247 rosin soldering flux and other residues are removed from electronic assemblies by means of terpene compounds in combination with terpene emulsifying surfactants by rinsing in water.

Complete removal of adhesive and other residues also pose a problem. During manufacture of electronic circuit assemblies components are mounted on the upper surface of the board with leads protruding downwardly through holes in the board and are secured to the bottom surface of the board by means of an adhesive. Further, sometimes it is necessary to temporarily protect certain portions of boards from processing steps such as the process of creating corrosion resistant gold connecting tabs at board edges. Such transient protection of portions of circuit boards can be achieved by application of special adhesive tape to susceptible areas. Once such protection no longer is needed, adhesive tape must be removed. In both instances, a residue of adhesive generally remains which, if not thoroughly removed, can cause premature board failure. Removal

of such adhesive residue traditionally has been carried out by use of chlorinated solvents which, as already described, are toxic and environmentally undesirable.

Thus, residual contaminants which are likely to be found on electronic circuit assemblies and which can be removed by compositions and methods of the present invention include, but are not limited to, for example, rosin flux, photoresist, solder masks, adhesives, machine oils, greases, silicones, lanolin, mold release, polyglycols and plasticizers.

Examples of excellent aqueous cleaning concentrates for cleaning circuit boards and wiring boards which are environmentally friendly and resolve many of the above problems of circuit board cleaning are disclosed in the U.S. Patent No. 5,431,847, issued to Winston et al. and assigned to Church & Dwight, Princeton, N.J. In addition to employing excellent surfactant cleaning ability of N-alkyl pyrrolidone derivatives in their concentrates, Winston et al. also employ other cleaning surfactants such as block copolymers of ethylene oxide and propylene oxide, alkoxylated alcohols, carboxylated alkylene oxide condensates of fatty alcohols, and the like to enhance cleaning properties of the compositions.

In the area of metal cleaning, similar environmental problems of waste from metal cleaning compositions occur. Although many existing solvents have shown to be good metal cleaners, such solvent cleaners generally employ various halogenated hydrocarbons and non-halogenated hydrocarbons. Such

cleaners are toxic to the environment and can be dangerous, especially in closed environments such as garages and the like or in home usage.

Non-halogenated hydrocarbon solvents employed in metal cleaning such as toluene and Stoddard solvent and like organic compounds such as ketones and alcohols generally are flammable, have high volatility and have dubious ability to be recycled for continuous use. These, plus unfavorable safety, environmental and cost factors, put this group of solvents in a category which is unattractive for practical consideration. Most useful organic solvents are classified as volatile organic compounds (VOCs) which pollute the atmosphere, promote formation of toxic ozone at ground level, and add to the inventory of greenhouse gases.

The present assignee, Church and Dwight, has a number of excellent aqueous cleaning compositions which resolve many of the above mentioned problems observed with many organic solvent and aqueous metal cleaners. Examples of excellent aqueous cleaners are disclosed in copending U.S. patent application Serial No. 08/311,268, assigned to Church & Dwight, which employ N-alkyl pyrrolidone derivatives along with other surfactants such as alkoxylated (thiol) surfactants, amine oxide surfactants, ethoxylated primary alkyl amines, and surfactants derived from condensation of ethylene oxide with a product resulting from a reaction of propylene oxide and ethylene diamine. Such aqueous cleaning compositions resolve many problems associated with

organic solvents and many aqueous metal cleaners.

Although the aqueous circuit board cleaners and aqueous metal cleaners discussed above are excellent for their cleaning and metal anticorrosion purposes, a problem associated with cleaning compositions containing N-alkyl pyrrolidone derivatives is corrosion of materials composed of plastic such as drain pipes from cleaning stations where precision cleaning of circuit and wiring boards occur, or stations such as parts washers employed to clean metal parts and the like. Also plastic piping and tubing are frequently found in spray washers to spray, deliver or recirculate cleaning compositions to clean circuit and wiring boards, and metal parts. Because of the corrosive action of N-alkyl pyrrolidone derivatives on plastic, the cleaning industry is discouraged from employing the good cleaning ability of cleaning compositions containing N-alkyl pyrrolidone derivatives.

Unused or new plastic, such as chlorinated polyvinyl chloride, is a shiny, gray and rigid polymer. Corrosion of plastic material can be observed by swelling, change in color or weight gain and invariably, by a change in shine of plastic. Under the worst conditions of N-alkyl pyrrolidone derivative corrosion, plastics completely plasticize and dissolve into solution. Under slightly better conditions, plastics turn dark brown throughout, swell, gain weight and become rubbery, thus becoming useless. If the plastic is under any pressure, cracking and splitting also are observed. Under the

very best corrosion prevention conditions, plastics retain their shine indefinitely.

Certain surfactants, such as alkoxylated alcohols, glycol ethers, and surfactants derived from sequential addition of ethylene oxide and propylene oxide to ethylenediamine, can slow down corrosion of plastic only but do not prevent corrosion. Consequently, plastics exposed to cleaning compositions containing such surfactants along with N-alkyl pyrrolidone derivatives eventually corrode and become useless.

Thus, there is a need for an improved aqueous alkali cleaning composition which employs the excellent cleaning ability of N-alkyl pyrrolidone derivatives, and prevents corrosion of plastics.

A primary objective of the present invention is to provide an aqueous alkali cleaning composition which employs N-alkyl pyrrolidone derivatives and prevents corrosion of plastics.

Another objective of the present invention is to provide an aqueous alkali cleaning composition which is effective to clean flux, grease oil and other contaminants from circuit and wiring boards without being excessively corrosive to a substrate and irritating to human skin, and is environmentally friendly.

A further objective of the present invention is to provide an aqueous alkali cleaning composition which effectively cleans grease, oil and other contaminants from a metal surface.

Still yet another objective of the present invention is to provide an aqueous alkali cleaning

composition which can be used effectively in immersion and impingement type parts washers to effectively remove grease, oil and other contaminants from metal parts and which is safe to use and not a hazard to the environment upon disposal.

Other objectives and advantages of the present invention are apparent from the disclosure which follows, and will become apparent to those of skill in the art upon practicing the present invention.

SUMMARY OF THE INVENTION

In accordance with the present invention, aqueous alkali cleaning compositions containing an N-alkyl pyrrolidone derivative, and specific ethylene oxide/propylene oxide block copolymers which prevent corrosion of plastic are provided. Advantageously, specific ethylene oxide/propylene oxide block copolymers employed in compositions of the present invention prevent N-alkyl pyrrolidone derivatives from corroding polymer plastics without compromising cleaning efficacy of N-alkyl pyrrolidone derivatives. Such aqueous alkali cleaning compositions are useful for removing rosin solder fluxes and other residues from electronic circuit board assemblies during fabrication of such boards. As a result, any possibility of premature circuit failure which might occur in absence of such cleaning is eliminated or greatly reduced. Cleaning efficacy of compositions of the present invention is such that printed wiring boards thus treated meet stringent U.S. Department of Defense specifications.

Additionally, aqueous alkali cleaning compositions of the present invention effectively clean metal surfaces, such as aluminum, copper, iron, and the like by removing oil, grease and other contaminants, while at the same time inhibiting corrosion of metal surfaces.

Further, compositions of the present invention are characterized as having low environmental impact, unlike chlorinated hydrocarbon solvents and highly alkaline cleaners that have heretofore been employed to clean printed wiring boards, printed circuit board and metal surfaces. For example, alkali metal carbonate and bicarbonate salts employed to practice the present invention are naturally occurring and environmentally benign. Accordingly, rinse water can be sewered without treatment and minimal, if any, treatment is needed to remove organics from wash water before sewering, thus eliminating a need for costly water treating.

BRIEF DESCRIPTION OF THE DRAWINGS

Efficacy of the present invention invention will be better understood by reference to Figs. 1-3 herein wherein test results of certain embodiments of the cleaning compositions of the present invention are illustrated.

Fig. 1 is a graph showing color change of CPVC test coupons treated with aqueous concentrates containing N-(n-octyl) 2 pyrrolidone.

Fig. 2 is a graph showing weight degradation for CPVC test coupons treated with aqueous concentrates containing N-(n-octyl) 2 pyrrolidone.

Fig. 3 is a bar graph contrasting cleaning ability of a cleaning concentrate of the present invention with cleaning concentrates outside the scope of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Aqueous alkali cleaning compositions of the present invention comprise an alkali metal salt, an N-alkyl pyrrolidone derivative and specific ethylene oxide/propylene oxide block copolymers which prevent N-alkyl pyrrolidone derivatives from corroding plastics. Many plastics which N-alkyl pyrrolidone derivatives corrode are found in drain pipes for disposing of cleaning solutions or jet sprays for applying cleaning solutions to clean circuit, wiring boards, or metal surfaces, and for pipes which recirculate cleaning solutions at cleaning stations.

The specific block copolymers prevent corrosion of plastic materials such as polyethers, polyesters and the like. Examples of such plastics include, but are not limited to, thermoplastics such as chlorinated polyvinyl chloride (CPVC), polycarbonate, vinylidene fluoride-hexafluoropropylene copolymer, ethylene propylene diene methylene copolymer, low density polyethylene terephathalate, polyvinyl chloride, and the like.

Essentially, aqueous alkali cleaning compositions of the present invention comprise mixtures of alkali metal salts which effectively remove flux from circuit and wiring boards. Accordingly, the term "flux removing" as used herein is intended to define the mixture of essentially active ingredients which comprises an alkali metal salt, an N-alkyl pyrrolidone derivative, a specific ethylene oxide/propylene oxide block copolymer, and any additional performance enhancers such as metal corrosion inhibitors and any other adjuvants such as additional surfactants, antifoam agents, etc. as hereinafter described.

The cleaning compositions or flux removing compositions preferably are formulated into concentrates. The terms "flux removing concentrated solutions" or "concentrates" as used herein define aqueous mixtures containing from about 5 to about 45, preferably, about 15 to about 30 percent by weight of flux removing compositions with the balance being essentially water.

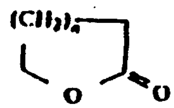
In addition to removing flux from circuit and wiring boards, the alkali cleaning compositions of the present invention are useful for removing any type of contaminant from a metal surface including grease, cutting fluids, drawing fluids, machine oils, antirust oils such as cosmoline, carbonaceous oils, sebaceous oils, particulate matter, waxes, paraffins, used motor oil, fuels, etc. Any metal surface can be cleaned including iron-based metals such as iron, iron alloys, e.g., steel, tin, aluminum, copper, tungsten, titanium, molybdenum, etc., for example. Structures of metal surfaces to

be cleaned can vary widely and are unlimited. Thus, the metal surface can be as a metal part of complex configuration, sheeting, coils, rolls, bars, rods, plates, disks, etc. Such metal components can be derived from any source including for home use, for industrial use such as for the aerospace industry, automotive industry, electronics industry, etc., wherein metal surfaces have to be cleaned.

As used herein the terms "flux removing solutions" or "flux removing solutions in use" are meant to define aqueous mixtures containing from about 0.1 to about 10 percent by weight of an alkali cleaning composition with the balance comprised essentially of water and which are solutions employed to clean circuit boards and metal surfaces. Also, as used herein, "flux removing composition" and "cleaning composition" have the same meaning since as stated previously, electronic circuit assemblies including printed circuit boards and printed wiring boards often contain residues other than fluxes which compositions of the present invention are able to remove and thus "flux removing composition" is intended as an all-purpose cleaner.

Any N-alky pyrrolidone derivative which can be employed as a surfactant is suitable to practice the present invention. Preferred N-alkyl pyrrolidone derivatives are N-(n-alkyl) pyrrolidones where an alkyl group contains from 6 to 22 carbon atoms. Most preferred pyrrolidones are N-(n-octyl) 2 pyrrolidone, N-(n-decyl) 2 pyrrolidone, N-(n-dodecyl) 2 pyrrolidone and N-(n-tetradecyl) 2 pyrrolidone. Such compounds are described in U.S. Pat. No. 5,093,031, assigned to ISP Investments,

Inc., Wilmington, DE, and is incorporated herein in its entirety by reference. Such N-alkyl pyrrolidone derivatives having a molecular weight of from about 180 to about 450 are conveniently prepared by several known processes including a reaction between a lactone having the following formula



wherein n is an integer from 1 to 3, and an amine having the formula $R'-NH_2$ wherein R' is a linear alkyl group having 6 to 20 carbon atoms; amines derived from natural products, such as coconut amines or tallow amines distilled cuts or hydrogenated derivatives of fatty amines. Also, mixtures of amine reactants can be used in the process for preparing pyrrolidone compounds.

Generally, C_6 to C_{14} alkyl pyrrolidones have been found to display primarily surfactant properties; whereas C_{16} to C_{22} alkyl species are primarily complexing agents; although some degree of surfactant and complexing capability exits in all such pyrrolidone species. N-(alkyl) pyrrolidone derivatives are employed in compositions of the present invention in amounts from about 0.1 to about 2.0 wt.%, preferably from about 1.0 to about 1.5 wt.% of a cleaning composition (without water).

Suitable alkaline salts or mixtures thereof employed to practice the present invention are those capable of providing a desired pH. Most suitable are salts of potassium, sodium and ammonium with potassium and sodium being preferred. Preferred are carbonates and bicarbonates and

mixtures thereof which are economical, safe and environmentally friendly. Most preferred are carbonate salts. Such carbonate salts include potassium carbonate, potassium carbonate trihydrate, sodium carbonate, sodium carbonate decahydrate, sodium carbonate heptahydrate, sodium carbonate monohydrate, sodium sesquicarbonate and double salts and mixtures thereof. Preferably, alkaline cleaning salts used in compositions are alkali metal carbonates or hydrates thereof present in amounts of from about 10 to about 70 wt.% of the composition (without water), preferably, about 25 to about 45 wt.%. Thus, alkali metal carbonates can comprise from 0 to about 70 wt.% potassium carbonate, more preferably, about 10 to about 25 wt.% and 0 to about 50 wt.% sodium carbonate, more preferably, 5 to about 20 wt.% of a composition (without water).

Bicarbonate salts preferably include potassium bicarbonate and sodium bicarbonate and mixtures thereof. Alkali metal bicarbonates can be present in amounts of 0 to about 60 wt.% of the composition (without water), preferably, about 15 to about 40 wt.%.

Other suitable alkaline salts include alkali metal ortho or complex phosphates. Complex phosphates are effective because of their ability to chelate water hardness and heavy metal ions. Complex phosphates include, for example, sodium or potassium pyrophosphate, tripolyphosphate and hexametaphosphates. Additional suitable alkaline salts useful in cleaning compositions of the present invention include alkali metal borates, acetates, citrates, tartrates, gluconates, succinates,

silicates, phosphonates, nitrilotriacetates, edates, etc.

Alkaline salts can be utilized in combination, and are used in concentrations such that resultant concentrates or solutions have a pH of from about 8 to less than 13, preferably from about 10 to less than 12 and, most preferably from about 10.9 to about 11.4. The desired pH of an aqueous cleaning composition can depend on types of contaminants removed. Thus, a lower pH range is desirable and effective for removing more easily removed contaminants. A pH of above 11.0 is preferred when removing more difficult to remove solder paste fluxes. However, at pHs of 12.6 and higher, solutions become increasingly toxic and corrosive to electronic circuit assemblies. Consequently, such high pH levels are preferably avoided. It is preferable that alkaline salts utilized in combination at dilution of a wash bath and at the desired pH also have an adequate reserve of titratable alkalinity, at least equivalent to about 0.2 to 4.5%, preferably from about 0.6 to 4.5% sodium hydroxide or caustic potash (potassium hydroxide), when titrated to the colorless phenolphthalein end point, which is at about pH 8.4 to maintain enhanced performance.

Alkali cleaning compositions of the present invention also comprise specific block copolymers of ethylene oxide/propylene oxide as plastic anticorrosion agents. Such specific block copolymers of ethylene oxide/propylene oxide are effective for preventing corrosion of certain plastics by N-alky pyrrolidone derivatives. Such

plastics typically are used to make drain pipes or tubing for cleaning apparatus where cleaning compositions containing N-alkyl pyrrolidone derivatives are employed. Specific block copolymers of ethylene oxide/propylene oxide suitable for practicing the present invention are based on addition of ethylene oxide and propylene oxide to a low molecular weight organic compound containing one or more active hydrogen atoms. Such block copolymers have a weight average molecular weight of from about 1500 to about 2500, and an HLB (hydrophile-lipophile balance) of about 1 to 7. Block copolymers capped with ethylene oxide (EO/PO/EO) have a hydrophile composition formed from the ethylene oxide or EO block of from about 5 to about 20 wt.%, preferably from about 5 to about 15 wt.% of the polymer. Block copolymers capped with propylene oxide (PO/EO/PO) have a hydrophobe composition formed from propylene oxide or PO block of from about 5 to about 20 wt.%, preferably from about 5 to about 15 wt.% of the polymers.

The specific polymers based on addition of ethylene oxide and propylene oxide to propylene glycol and ethylene glycol are commercially available under the names Pluronic® and Pluronic® R from BASF Wyandotte Corporation of Wyandotte, Michigan. Pluronic® is based on addition of propylene oxide to two hydroxyl groups of propylene glycol followed by ethylene oxide addition to sandwich the propylene oxide hydrophobe between the ethylene oxide hydrophilic groups.

The structure is:

(1)

$$HO-(CH_2CH_2O)_x-(CH_2\underset{\displaystyle |}{\overset{CH_3}{\overset{|}{C}}}HO)_y-(CH_2CH_2O)_x-H$$

Pluronic® R is based on addition of ethylene oxide to ethylene glycol followed by propylene oxide addition to sandwich the ethylene oxide hydrophile between the propylene oxide hydrophobic groups.

The structure is:

(2)

$$HO-(\overset{CH_3}{\overset{|}{C}}HCH_2O)_x-(CH_2CH_2O)_y-(CH_2\overset{CH_3}{\overset{|}{C}}HO)_x-H$$

where x and y in each of the above general formulas are integers such that the block copolymer has a molecular weight of from about 1500 to about 2500. Preferred specific ethylene oxide/propylene oxide block copolymers are based on addition of propylene oxide to two hydroxyl groups of propylene glycol followed by ethylene oxide to sandwich the hydrophobe between ethylene oxide hydrophilic groups (formula 1) with a hydrophile percent of about 10 and a molecular weight of about 2000. An example of such a block copolymer is Pluronic L61. Another preferred specific ethylene oxide/propylene oxide block copolymer is based on addition of ethylene oxide to ethylene glycol followed by propylene oxide addition to sandwich the hydrophile between hydrophobic groups (formula 2) with a hydrophobe percent of about 10 and a molecular weight of about 2000. An example of such a block copolymer is

Pluronic 17R1. Such specific block copolymers can be prepared by various methods known in the art.

While not wishing to be held to any particular theory, it is believed that the specific ethylene oxide/propylene oxide block copolymers form an intermolecular equilibrium relationship with N-alkyl pyrrolidone derivatives where specific block copolymers of ethylene oxide/propylene oxide form a temporary micelle structure around N-alkyl pyrrolidone for a period of time long enough to prevent corrosion of plastic materials but releasing N-alkyl pyrrolidone derivatives for a sufficient amount of time to clean effectively. An alternative theory is that hydrophilic portions of N-alkyl pyrrolidone derivatives significantly interact by intermolecular forces, such as Van der Waals forces, with the specific block copolymers of ethylene oxide/propylene oxide, while minimally interacting with hydrophobic portions of N-alkyl pyrrolidone derivative molecules. Such interaction allows hydrophobic portions of N-alkyl pyrrolidone derivatives sufficient time to effectively clean, but not enough time to corrode plastic material.

To protect plastic parts from corrosion effects of N-alkyl pyrrolidone derivatives, the specific block copolymers of ethylene oxide/propylene oxide are included in cleaning compositions of the present invention in amounts of from about 0.5 to about 10 wt.% of a composition (without water), or from about 5.0 to about 7.1 times the weight of N-alkyl pyrrolidone derivatives added to a cleaning composition. Preferably, the specific block copolymers of ethylene

oxide/propylene oxide are added in amounts of from about 1.0 to about 5 wt.%, most preferably from about 1.5 to about 3.0 wt.% of cleaning compositions (without water).

Alkaline compositions of the present invention can contain one or more additional corrosion inhibitors to prevent corrosion or pitting of connecting tabs or solder joints, metals or other materials present on circuit boards. Such additional anticorrosion agents include, but are not limited to, water soluble magnesium salts such as magnesium sulfate, magnesium nitrate, magnesium oxide and the like, and alkali metal silicate salts, such as sodium and potassium silicate salts.

Alkali metal silicates which are used can be in a variety of forms which can be encompassed generally by the formula $M_2O:SiO_2$ wherein M represents an alkali metal and in which the ratio of two oxides can vary. Most useful alkali metal silicates have an M_2O to SiO_2 mole ratio of between 1:0.5 to 1:4.5. Most preferably, the M_2O to SiO_2 ratio is between 1:1.6 and 1:4.0. Such silicates also provide additional alkalinity to wash water to help cleaning, and to promote brightness and shininess of solder joints. For sufficient corrosion protection, it is useful to add 0.1 to 25 wt.% of silicate corrosion inhibitor based on the amount of cleaning composition (without water). To enhance brightening, it has been found useful to include at least 10 wt.% silicate in compositions and, preferably, amounts of silicate greater than 15 wt.% can be used to ensure brightening of metal parts and removal of all white residues which tend

to collect on metal components including solder joints.

At a pH below about 11.0 silicate can begin to precipitate from aqueous solutions such as a dilute wash bath. Silicate precipitation from aqueous concentrates of cleaning compositions also can occur. To aid in keeping silicate in solution, an anionic polymer can be added to the compositions.

Anionic homopolymers or copolymers with molecular weights between about 1,000 to about 5,000,000 or mixtures thereof can be employed in this invention as silicate stabilizers. Optimal polymers are ones which dissolve easily and do not increase solution viscosity to excessive levels when added at concentrations required for optimum silicate stability.

The following anionic polymers are non inclusive examples of those suitable for stabilizing silicate solutions according to this invention: carboxymethylcellulose, polyacrylic acid, polymethacrylic acid, polymaleic acid, polyglycolic acid, heteropolymers of acrylic and methacrylic acid, xanthan gum, carrageenan gum and alginate gum. In alkaline concentrates or solutions of the present invention, anionic polymers are present essentially in the form of the sodium or potassium salts thereof. Additional alkali can be added to neutralize the polymers.

Preferably, polyacrylic acids, such as in the form of sodium polyacrylate in solution, can be employed as solder silicate stabilizing agents. Polyacrylates used in this embodiment preferably have molecular weight of between about 100,000 and

4,000,000, preferably from over 150,000 to 4,000,000. An especially preferred molecular weight range is about 250,000 to 2,000,000. Examples of such polymers are marketed under the tradename "Carbopol", from B.F. Goodrich. It is believed that anionic polymers which are particularly useful in this invention form stable solutions or suspensions in water and have a folded or cross-linked structure which provides a three-dimensional porous matrix in solution. Pores in this matrix have an adequate size to entrap alkali metal silicates.

Relatively small amounts of the anionic polymer are effective. Thus, at a pH below 11.0 and at silicate concentrations of about 0.5 to about 10.0 wt.% in a cleaning concentrate, amounts of polyacrylic acid needed for stabilization range from about 0.1 to 2 wt.%. When amounts of silicate ranging from about 1-8 wt.% are employed in concentrates, about 0.3 to about 1.2 wt.% of polyacrylic acid stabilizer is used relative to the concentrates.

It also is useful to include at least one antifoam agent in any of the cleaning compositions of the present invention. Antifoam agents are utilized to prevent formation of excessive foam caused by rosin flux/flux removing combinations. Presence of foam interferes with mechanical action of cleaning equipment used to wash circuit boards. It is important, if not critical, that antifoam agents used herein do not act by replacing flux film with another residual surface film which can affect performance of an electronic circuit board in use. Antifoam agents can be agents which solely act to

inhibit foam, or can be a surfactant which help clean boards and emulsify soils.

Preferred examples of antifoam agents include compounds formed by condensing ethylene oxide with a hydrophobic base formed by condensation of propylene oxide with propylene glycol. Hydrophobic portions of the molecule which exhibit water insolubility have a molecular weight of from about 1,500 to 1,800. Addition of polyoxyethylene radicals to such hydrophobic portions tend to increase water solubility of the molecule as a whole and the liquid character of the product is retained up to a point where polyethylene content is about 50 percent of the total weight of the condensation product. Examples of such compositions are the "Pluronics" sold by BASF - Wyandotte. Such compounds also enhance flux removal.

Other suitable antifoam agents that also enhance flux removal include: Polyethylene oxide/polypropylene oxide condensates of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide/propylene oxide, ethylene oxide being present in amounts equal to 1 to 25 moles of ethylene oxide per mole of alkyl phenol and propylene oxide being present in amounts equal to 1 to 25 moles of propylene oxide per mole of alkyl phenol. Alkyl substituents in such compounds can be derived from polymerized propylene, diisobutylene, octene, or nonene, for example.

Also suitable are compounds derived from condensation of ethylene oxide with the product

resulting from reaction of propylene oxide and ethylene-diamine or from the product of the reaction of a fatty acid with sugar, starch or cellulose. For example, compounds containing from about 40 percent to about 80 percent polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, and hydrophobic bases having a molecular weight on the order of 2,500 to 3,000 are satisfactory.

In addition, condensation products of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide and propylene oxide, e.g., a coconut alcohol-ethylene oxide-propylene oxide condensate having from 1 to 30 moles of ethylene oxide per mole of coconut alcohol, and 1 to 30 moles of propylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms, also can be employed.

Antifoam agents of the present invention preferably are employed in flux removing compositions (without water) at about 0.01 to about 10 wt.% and in flux removing concentrates in amounts of up to about 1.0 percent by weight, preferably, about 0.10 to about 0.50 percent by weight based on the total weight of the aqueous flux removing concentrate. Thus, antifoam agents can be included in flux removing compositions, aqueous concentrates or added directly to aqueous wash baths as long as

addition results in desired concentration during use.

In addition to N-alkyl pyrrolidone derivatives, the present invention also contemplates use of other surfactants in aqueous cleaning-solutions in order to enhance wetting and emulsifying ability of cleaning solutions and permit maximum penetration thereof within regions of circuit boards most difficult to clean. Additional surfactants used can be agents also used to control foam. Suitable surfactants include anionic, nonionic, anionic surfactants or amphoteric surfactants or combinations thereof. Surfactants preferably are soluble, stable and, preferably, nonfoaming in use. A combination of surfactants can be employed. The term "surfactant", as used herein, can include other forms of dispersing agents or aids.

It has been found especially effective to use alkoxylated alcohols which are sold under the tradename of "Polytergent SL-Series" as surfactants, such as Polytergent SL 42 by Olin Corporation. Also, polycarboxylated ethylene oxide condensates of fatty alcohols manufactured by Olin under the tradename of "Polytergent CS-1" have been found effective, especially in combination with the above Polytergent SL-Series surfactants. An effective surfactant which also provides antifoam properties are alkoxylated linear alcohols such as "Polytergent SLF-18" also manufactured by Olin. A combination of this surfactant together with the above two surfactants has been found to provide excellent cleaning with low foam.

Ethoxylated alcohols with 8 to 20 carbons, such as those containing from 3 to 30 moles of ethylene oxide per mole of alcohol also can be used as surfactants in this invention. A preferred method of preparing such low foaming surfactants is by end-capping an ethoxylated alcohol with propylene oxide. Monocarboxylated derivatives of such surfactants also can be used.

Sodium or potassium salts of sulfonated benzene or naphthalene derivatives such as alkyl benzene sulfonate, or alkyl naphthalene sulfonate or disulfonate can be used. However, caution preferably is employed as such surfactants can impart excessive uncontrollable foam to the wash water.

Amount of surfactants utilized range from about 1 to about 15 wt.% of the composition but can vary depending on conditions and contamination encountered, and higher surfactant levels can be employed if so desired. Preferably, surfactant comprises from about 5 to about 10 wt.% of the composition.

A hydrotrope can be included to help solubilize any organic adjuvants such as surfactants, anti-foam agents, etc. which are contained in salt-containing concentrates. Hydrotrope is present in amounts of from about 2 to about 15 wt.% preferably from about 8 to about 12 wt.% of a composition (without water). Preferred hydrotropes comprise alkali metal salts of intermediate chain length monocarboxylic fatty acids, i.e., C_7-C_{13}. Other adjuvants also can be

added to improve properties or performance of the aqueous cleaning compositions.

It has been found that concentrates of the present invention preferably be prepared hot for example at between about 50 to about 90°C. Polymers first are dissolved in water. This can be facilitated using a homogenizer. Silicate then is added as a concentrated solution. Alkaline salts then are added, followed by surfactants and other ingredients.

Aqueous cleaning solutions which are employed in cleaning procedures described herein usually contain from about 0.1 to about 10, or more, weight percent, preferably, from about 0.6 to about 5 weight percent and, most preferably, from about 1 to 3 weight percent of a cleaning composition of the present invention with the balance being water. An upper limit of concentration of cleaning composition is not critical and is determined by fabrication conditions, amount of residues and difficulty of removing same from circuit assemblies, etc. Preferably, deionized water is used for both solutions and, as well, concentrates of the present invention.

Applicability of compositions of the present invention to various aspects of printed circuit/wiring board fabrication processes can best be understood by a description of a representative assembly process.

An assembly manufacturing process involves placement of components such as integrated circuits, resistors, capacitors, diodes, etc. on a board's or insertion through pre-drilled holes. Components

then are secured by soldering, by mechanical or automatic means. Interspersed with soldering operations are cleaning procedures and inspections to ensure that tape and solder flux residues which can lead to premature circuit failure do not remain.

For removal of rosin soldering flux deposits and other residues during printed circuit/wiring board fabrication, compositions of the present invention can be applied to boards by immersion in dip tanks or by hand or mechanical brushing. Alternatively, such compositions can be applied by any commercially available printed wiring board cleaning equipment. Dishwasher size units can be employed, or much larger cleaning systems such as "Poly-Clean +" and various "Hydro-Station" models produced by Hollis Automation, Inc. of Nashua, New Hampshire.

Depending upon their design, such washers can apply cleaning compositions of the present invention by spraying with mechanical nozzles or by rolling contact with wetted roller surfaces. Temperatures at which compositions can be applied can range from room, or ambient, temperature (about 70°F.) to about 180°F., preferably, about 140° to 170°F. Cleaning compositions or concentrates are diluted with water from as low as about 0.1 percent by weight (or volume) concentration to up to about 10 percent by weight.

Once solder flux has been loosened and removed during a period of contact which typically ranges from about 1 to about 5 minutes, but can be up to about 10 minutes circuit/wiring boards are taken from the flux removing solution. Another

advantage of the instant invention is that cleaning solutions need not be flushed with solvents as with many other currently employed processes using organic solvents or strong alkaline aqueous compositions. Herein, boards can simply be flushed with water for a period of up to about 2 minutes. Deionized water is preferred. Optimal rinsing time varies according to kinds of surfactants and concentrations of cleaning solutions used and can easily be determined by routine experimentation. Advantageously, cleaning compositions of the present invention can be recycled through circuit board cleaning apparatus and reused for further cleaning without fear that such cleaning compositions cause corrosion of plastic parts of the apparatus. Any chance of corrosion is prevented by employing block copolymers of ethylene oxide/propylene oxide as described above. Because plastic components of cleaning apparatus are protected from corrosion by N-alkyl pyrrolidone derivatives, cleaning solutions of the present invention advantageously can employ the superior cleaning abilities of N-alkyl pyrrolidone derivatives.

Cleaned boards then are dried, preferably with forced air. Drying is expedited if the air is warmed, preferably to above about 100°F.

Efficacy of rosin soldering flux removal from printed wiring boards is such that the boards meet stringent military specifications for low resistivity after cleaning. For example, such boards meet the MIL-P-28809A standard for low resistivity of solvent extracts resulting when contamination has been removed from a circuit board

cleaned according to MIL-P-55110C. Resistivity of such solvent extracts after cleaning boards is complete is most easily determined with an Omega Meter. Omega meter is the registered trademark of Kenco Industries, Inc., Atlanta, GA, for a microprocessor-controlled contamination test system that rapidly measures changes in resistivity due to contaminating ions.

Results of Omega Meter measurements are expressed in equivalent units of ug $NaCl/in^2$ or its metric equivalent. According to MIL-P-28809A, an acceptable resistivity value for a cleaned board is equivalent to about 2.2 ug $NaCl/cm^2$ or about 14 ug $NaCl/in^2$, but far better results are routinely obtained after solder flux has been removed with cleaning solutions of the present invention as disclosed in Example II.

Cleaning solutions of the present invention also are effective in removing other undesirable and deleterious substances and residues. One particularly troublesome substance is residue left by adhesive tape used during fabrication of electronic circuit assemblies.

During the process of gold plating connecting tabs to improve corrosion resistance, tin-lead residues must first be removed from any unplated tabs. Removal of these residues is carried out by use of etching chemicals that can damage other unprotected printed circuit/wiring board components. To protect vulnerable components from etching chemicals, boards are wrapped on both sides with an adhesive plating tape which forms a shield or splash guard for all but exposed tab areas.

Etching chemicals then remove any tin-lead residues on any tabs, a nickel plate is applied as a base for gold, and gold plating of the tabs finally is carried out. Adhesive plating tape which is maintained in place through all of these etching and plating steps, then is removed. When the tape is removed following the nickel and gold plate step, it is at this point that cleaning compositions of the present invention can be used.

Thus, following removal of the tape, a silicone-based and/or rubber-based adhesive residue can remain on a board. Such residue easily can be removed by employing compositions of the present invention under the same conditions described above for solder flux removal. Exact operational parameters will be determined by the nature of adhesive residue and the tenacity with which it adheres to a board, but conditions as described above generally are effective. As in the case of solder flux removal, treatment of a board with aqueous alkali cleaning solutions of the present invention is followed generally by water flushing and air drying.

Efficiency of removal of adhesive residues from printed circuit/wiring boards by compositions of the present invention is such that no residues are visible after cleaning. A simple 5-10X stereomicroscope can facilitate visual inspection for tape residues following cleaning.

The disclosure presented above is primarily concerned with electronic circuit assembly cleaners. It is to be well understood that the present invention also is directed to any aqueous

cleaner in which the cleaning composition or aqueous cleaning concentrate comprises alkaline cleaning salts, an N-alkyl pyrrolidone to boost detersive action, and a specific block copolymer of ethylene oxide/propylene oxide having a molecular weight of from about 1500 to about 2500 as an anticorrosion agent. Useful products other than circuit board cleaning compositions as described above include laundry detergents, automatic dishwashing liquids, metal cleaning, carpet shampoos, floor tile cleaners, etc.

Many modifications and variations of the present invention can be made without departing from its spirit and scope, as will become apparent to those skilled in the art. The following examples are provided to further illustrate the present invention and are not intended to limit the scope of the present invention.

Example I

To illustrate anticorrosion activity of aqueous alkali cleaning concentrates of the present invention on chlorinated polyvinyl chloride (CPVC) test coupons, eight cleaning concentrates were prepared. Aqueous cleaning concentrates tested are listed in Tables 1 and 2.

Twenty four CPVC test coupons of 3/4"x4"x1/8" were weighed. Three coupons each were submerged in each of eight concentrates disclosed in Tables 1 and 2 at 150 degrees F for periods of 24, 120 and 240 hours with each concentrate stirred at 600 rpm. Eight coupons were removed from each concentrate after time periods of 24, 120 and 240

hours; dried for 1 hour at 80 degrees C; allowed to cool; re-weighed; measured for percent swelling by measuring change in the length, width and height of each coupon; and measured for color change on a colorimeter. Total average color change and total weighted degradation of each coupon are graphically displayed in Figures 1 and 2, respectively.

Color change is based on a three-dimensional scale which consists of color change of a material on a from black to white scale, a from green to red scale, and a from blue to yellow scale. Color change of a sample material is expressed by equation $\Delta E=(L^2+a^2+b^2)^{½}$ where variables L, a, and b represent a material's color change in the from black to white, from green to red, and the from blue to yellow regions, respectively. A colorimeter measures such changes of a test material under simulated conditions of total color change in incandescent light, total color change in north sky daylight (sunny day), and total color change in fluorescent light; and generates a repeatable number ΔE or total average color change in units of "total color change." Average total color change for each coupon is plotted on the graph in FIG. 1.

Average total color change values of 3 or below indicate that a CPVC test coupon showed no signs of corrosion, while numerical values above 3 clearly indicate corrosion on CPVC test coupons. Because all scientific measurements have some degree of error, the numerical zero point on the graph is not the statistically true zero point. The numerical value of 3 was determined as the "wobble" point, or the statistically true "0" point where no

corrosion is observable. Such "wobble" points are determined visually by observing at what point test samples of CPVC show corrosion or noticeable physical change or noticeable beginning of change in appearance when treated in a solution similar to solution A in Table 1 (absent Pluronic L61) for 24 hours.

Coupons treated in concentrate A which contained an ethylene oxide/propylene oxide block copolymer with a molecular weight of about 2000 (Pluronic L61) did not show any color change after 24 hours, 120 hours, or 240 hours. In contrast, coupons treated in concentrates without Pluronic L61 (concentrates B to H) show considerable color change after 120 hours and 240 hours, thus clearly showing evidence of corrosion. Further, test coupons treated in test solutions B, C, D, F and H were extremely visibly corroded after 120 hours such that tests were not carried out in these solutions for a 240 hour time period.

Figure 2 further supports the superior anticorrosion action of cleaning concentrates of the present invention. Total weighted degradation of each test coupon was determined by adding the change in weight of each coupon plus the percent swell of each coupon and ΔE for each coupon in a given test concentrate to determine an arbitrary number to represent the total weighted degradation of each test coupon. The "Wobble" point for total weighted degradation was determined to be about 10.0. Thus, numerical values for coupons exceeding about 10.0 show corrosion. Coupons treated in concentrate A definitely showed no weight degradation after 24

hours, 120 hours, or 240 hours. In contrast, coupons treated in the other test concentrates all showed corrosion by 120 hours of treatment except for coupons treated in solution G, but by 240 hours of treatment such coupons showed definite corrosion. Thus, the results of the test concentrates clearly show that the specific ethylene oxide/propylene oxide block copolymers of the present invention prevent corrosion of chlorinated polyvinyl chloride in contrast to concentrates which do not contain such block copolymers.

TABLE 1
CONCENTRATED FORMULAS (% WEIGHT)

Ingredient	A	B	C	D
Water	81.47	74.78	95.680	95.510
Sodium Hydroxide	0.28	0.68	0.068	0.042
Plurafac RA40[1]	0.00	0.00	2.000	0.000
Potassium Carbonate	5.15	7.81	0.781	0.773
Sodium Carbonate	4.55	6.90	0.690	0.683
Kasil #1 (29.1% sol.)[2]	3.12	4.73	0.473	0.468
Monatrope 1250[3]	2.75	2.15	0.215	0.413
Polytergent CS-1	0.04	0.05	0.005	0.006
Polytergent S405LF[4]	0.10	0.15	0.015	0.015
Polytergent SL42	0.23	0.35	0.035	0.035
Surfadone LP100[5]	0.35	0.40	0.040	0.053
Pluronic L61	2.00	0.00	0.000	0.000
Pluronic L31[6]	0.00	2.00	0.000	0.000
Pluronic 31R1[7]	0.00	0.00	0.000	2.000

1. Tradename for an alkoxylated surfactant alcohol manufactured by BASF Corporation.
2. Potassium silicate
3. Tradename for an intermediate chain-length monocarboxylic fatty acid.
4. Tradename for a biodegradable alkoxylated linear alcohol manufactured by Olin Corporation.
5. N-(n-octyl) 2 pyrrolidone surfactant.
6. Tradename for an ethylene oxide/propylene oxide copolymer with a M.W. of about 1100 and 10% hydrophile manufactured by BASF Corporation.
7. Tradename for a reverse ethylene oxide/propylene oxide copolymer with a M.W. of about 3250 and 10% hydrophile manufactured by BASF Corporation.

TABLE 2
CONCENTRATED FORMULAS (%WEIGHT)

Ingredient	E	F	G	H
Water	74.78	81.43	95.680	95.510
Sodium Hydroxide	0.68	0.28	0.068	0.042
Potassium Carbonate	7.81	5.15	0.781	0.773
Sodium Carbonate	6.90	4.55	0.690	0.683
Kasil #1 (29.1% sol.)	4.73	3.12	0.473	0.468
Monatrope 1250	2.15	2.75	0.215	0.413
Polytergent CS-1	0.05	0.04	0.005	0.006
Polytergent S405LF	0.15	0.10	0.015	0.015
Polytergent SL42	0.35	0.23	0.035	0.035
Polytergent SLF18	0.00	0.00	2.000	0.000
Surfadone LP100	0.40	0.35	0.040	0.053
Pluronic L61	0.00	0.00	0.000	0.000
Industrol-DW5[1]	2.00	0.00	0.000	0.000
Pluronic L92[2]	0.00	2.00	0.000	0.000
Tetronic 150R1[3]	0.00	0.00	0.000	2.000

1. Tradename for a low foaming, alcohol alkoxylate surfactant, BASF Corporation.
2. Tradename for an ethylene oxide/propylene oxide block copolymer with a M.W. of about 3725 and 20% hydrophile.
3. Tradename for a block copolymer surfactant based on addition of propylene oxide and ethylene oxide to ethylene diamine, BASF Corporation.

Example II

Four separate cleaning concentrates listed in Table 3 each were used to wash three separate sets of wiring boards except for cleaning concentrate I which was used to clean only two sets of boards. Each wiring board was soldered at 226 degrees C, and was washed with one of the four concentrates at 155 degrees F for 7 minutes. The cleaning system employed was a "Poly-clean +" machine manufactured by Hollis Automation, Inc. of Nashua, New Hampshire. Cleaning results of each set and the average of the sets for a given concentrate were determined and are shown in Figure 3.

Figure 3 is a bar graph showing ionic contamination of boards washed in one of four concentrates of Table 3. The white bars show ionic contamination of each individual board washed in one of the four concentrates. The hatched bars show the average ionic contamination of all boards washed in a particular concentrate. The results in Figure 3 show that wiring boards cleaned with composition L, which includes Pluronic L61 (ethylene oxide/propylene oxide block copolymer with a M.W. of about 2000 and 10% hydrophile), contain no contamination after cleaning, i.e., absence of any bars, in contrast to wiring boards washed in concentrates not containing Pluronic L61. Thus, in addition to preventing corrosion of CPVC, compositions of the present invention also show excellent cleaning ability.

TABLE 3
CLEANING CONCENTRATES (WEIGHT %)

Ingredient	I	J	K	L
Water	75.48	83.20	76.29	78.68
Sodium Hydroxide	0.68	0.28	0.28	0.28
Carbopol 625	0.90	0.00	0.90	0.00
Potassium Carbonate	7.81	5.15	7.81	5.15
Sodium Carbonate	6.90	4.55	6.90	4.55
Kasil #1 (29.1% sol.)	4.73	3.12	4.73	3.12
Monatrope 1250	2.15	2.72	2.15	2.75
Polytergent CS-1	0.05	0.04	0.05	0.04
Polytergent S405LF	0.15	0.10	0.15	0.10
Polytergent SL42	0.35	0.23	0.35	0.23
Polytergent SLF18	0.40	0.26	0.39	0.26
Surfadone LP100	0.40	0.35	0.00	0.35
Pluronic L61	0.00	0.00	0.00	2.00

WHAT IS CLAIMED IS:

1. An aqueous alkali cleaning composition comprising an alkali metal salt, an N-alkyl-pyrrolidone derivative surfactant, and an ethylene oxide/propylene oxide block copolymer having a molecular weight of from about 1500 to about 2500.

2. The aqueous alkali cleaning composition of claim 1, wherein the ethylene oxide/propylene oxide block copolymer has the following formula

$$HO-(CH_2CH_2O)_x-(CH_2\underset{}{\overset{CH_3}{\overset{|}{C}}}HO)_y-(CH_2CH_2O)_x-H$$

wherein x and y are integers such that the block copolymer has a molecular weight of from about 1500 to about 2500.

3. The aqueous alkali cleaing composition of claim 2, wherein ethylene oxide comprises from about 5 to about 15 wt.% of the block copolymer.

4. The aqueous alkali cleaning composition of claim 2, wherein the block copolymer has a molecular weight of about 2000 and an ethylene oxide percent of about 10.

5. The aqueous alkali cleaning composition claim 1, wherein the ethylene oxide/propylene oxide block copolymer has the following formula

$$HO-(\overset{CH_3}{\overset{|}{C}}HCH_2O)_x-(CH_2CH_2O)_y-(CH_2\overset{CH_3}{\overset{|}{C}}HO)_x-H$$

wherein x and y are integers such that the block copolymer has a molecular weight of from about 1500 to about 2500.

6. The aqueous alkali cleaning composition of claim 5, wherein propylene oxide

comprises from about 5 to about 15 wt.% of the block copolymer.

7. The aqueous alkali cleaning composition of claim 5, wherein the block copolymer has a molecular weight of about 2000 and propylene oxide percent of about 10.

8. The aqueous alkali cleaning composition of claim 1, wherein the alkali metal salts comprise carbonate salts, bicarbonate salts, or mixtures thereof.

9. The aqueous alkali cleaning composition of claim 1, wherein the N-alkyl pyrrolidone derivative comprises an N-(n-alkyl) 2 pyrrolidone.

10. The aqueous alkali cleaning composition of claim 9, wherein the N-(n-alkyl) 2 pyrrolidone comprises N-(n-octyl) 2 pyrrolidone, N-(n-decyl) 2 pyrrolidone, N-(n-dodecyl) 2 pyrrolidone, or N-(n-tetradecyl) 2 pyrrolidone.

11. The aqueous alkali cleaning composition of claim 1, further comprising a metal anticorrosion agent.

12. The aqueous alkali cleaning composition of claim 11, wherein the metal anticorrosion agent comprises magnesium salt, silicate salt or mixtures thereof.

13. The aqueous alkali cleaning composition of claim 1, wherein the ethylene oxide/propylene oxide block copolymer comprises from about 0.5 to about 10.0 wt.% of the composition.

14. The aqueous alkali cleaning composition of claim 1, comprising an additional surfactant.

15. The aqueous alkali cleaning composition of claim 14, wherein the additional surfactant is an alkoxylated alcohol.

16. The aqueous alkali cleaning composition of claim 14, wherein the additional surfactant is a polycarboxylated ethylene oxide condensate of a fatty alcohol.

17. The aqueous alkali cleaning composition of claim 1, further comprising a hydrotrope.

18. The aqueous alkali cleaning composition of claim 17, wherein the hydrotrope comprises an alkali metal salt of an intermediate chain length monocarboxylic fatty acid.

19. An aqueous alkali cleaning concentrate comprising an alkali cleaning composition, wherein the cleaning composition comprises from about 5 to about 45 wt.% of the concentrate, the balance water, wherein an alkali metal salt comprises from about 10 to about 70 wt.% of the composition, an N-alkyl pyrrolidone derivative surfactant comprises from about 0.1 to about 2.0 wt.% of the composition, a metal anticorrosion inhibitor comprises from about 0.1 to about 25 wt.% of the composition, and further comprising an ethylene oxide/propylene oxide block copolymer having a molecular weight of from about 1500 to about 2500.

20. The concentrate of claim 19, wherein the block copolymer has the following formula

$$HO-(CH_2CH_2O)_x-(CH_2\overset{\displaystyle CH_3\atop|}{C}HO)_y-(CH_2CH_2O)_x-H$$

where x and y are integers such that the block copolymer has a molecular weight of from about 1500 to about 2500.

21. The concentrate of claim 20, wherein ethylene oxide comprises from about 5 to about 15 wt.% of the copolymer.

22. The concentrate of claim 20, wherein the block copolymer has a molecular weight of about 2000 and an ethylene oxide percent of about 10.

23. The concentrate of claim 19, wherein the block copolymer has the following formula

$$HO-(\underset{\displaystyle CH_3}{\overset{|}{C}}HCH_2O)_x-(CH_2CH_2O)_y-(CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HO)_x-H$$

where x and y are integers such that the block copolymer has a molecular weight of from about 1500 to about 2500.

24. The concentrate of claim 23, wherein propylene oxide comprises from about 5 to about 15 wt.% of the copolymer.

25. The concentrate of claim 23, wherein the block copolymer has a molecular weight of about 2000 and a propylene oxide percent of about 10.

26. The concentrate of claim 19, wherein the alkali metal salts comprise carbonate salts, bicarbonate salts or mixtures thereof.

27. The concentrate of claim 19, further comprising an additional surfactant.

28. The concentrate of claim 27, wherein the additional surfactant is an alkoxylated alcohol.

29. The concentrate of claim 27, wherein the additional surfactant is a polycarboxylated ethylene oxide condensate of a fatty alcohol.

30. The concentrate of claim 19, further comprising a hydrotrope.

31. The concentrate of claim 30, wherein the hydrotrope comprises an alkali metal salt of an intermediate chain length monocarboxylic fatty acid.

32. The concentrate of claim 19, wherein the metal corrosion inhibitor comprises magnesium salts, silicate salts or mixtures thereof.

33. The concentrate of claim 19, wherein the N-alkyl pyrrolidone derivative comprises an N-(n-alkyl) 2 pyrrolidone.

34. The concentrate of claim 33, wherein the N-alkyl pyrrolidone derivatives comprises N-(n-octyl) 2 pyrrolidone, N-(n-decyl) 2 pyrrolidone, N-(n-dodecyl) 2 pyrrolidone, or N-(n-tetradecyl) 2 pyrrolidone.

35. The concentrate of claim 19, wherein the ethylene oxide/propylene oxide block copolymer ranges from about 0.5 to about 10 wt.% of the composition.

36. An aqueous alkali cleaning solution comprising an alkali cleaning composition, wherein the composition comprises from about 0.1 to about 10 wt.% of the solution, wherein an alkali metal salt comprises from about 10 to about 70 wt.% of the composition, a metal anticorrosion inhibitor comprises from about 0.1 to about 25 wt.% of the composition, an N-alkyl pyrrolidone derivative surfactant comprises from about 0.1 to about 20 wt.% of the composition, and further comprising an ethylene oxide/propylene oxide block copolymer with a molecular weight of from about 1500 to about 2500.

37. The aqueous solution of claim 36, wherein the ethylene oxide/propylene oxide block copolymer has the following formula

$$HO-(CH_2CH_2O)_x-(CH_2\underset{|}{\overset{CH_3}{C}}HO)_y-(CH_2CH_2O)_x-H$$

where x and y are integers such that the block copolymer has a molecular weight of from about 1500 to about 2500.

38. The aqueous solution of claim 37, wherein ethylene oxide comprises from about 5 to about 15 wt.% of the block copolymer.

39. The aqueous solution of claim 37, wherein the block copolymer has a molecular weight of from about 2000 to about 2500 and an ethylene oxide percent of about 10.

40. The aqueous solution of claim 36, wherein the ethylene oxide/propylene oxide block copolymer has the following formula

$$HO-(\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2O)_x-(CH_2CH_2O)_y-(CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HO)_x-H$$

where x and y are integers such that the block copolymer has a molecular weight of from about 1500 to about 2500.

41. The aqueous solution of claim 40, wherein propylene oxide comprises from about 5 to about 15 wt.% of the block copolymer.

42. The aqueous solution of claim 40, wherein the block copolymer has a molecular weight of from about 2000 to about 2500 and propylene oxide percent of about 10.

43. The aqueous solution of claim 36, wherein the alkali metal salts comprise carbonate salts, bicarbonate salts or mixtures thereof.

44. The aqueous solution of claim 36, wherein the N-alkyl pyrrolidone derivative comprises an N-(n-alky) 2 pyrrolidone.

45. The aqueous solution of claim 44, wherein the N-(n-alkyl) 2 pyrrolidone comprise N-(n-octyl) 2 pyrrolidone, N-(n-decyl) 2 pyrrolidone, N-(n-dodecyl) 2 pyrrolidone, or N-(n-tetradecyl) 2 pyrrolidone.

46. The aqueous solution of claim 36, further comprising an additional surfactant.

47. The aqueous solution of claim 46, wherein the additional surfactant is an alkoxylated alcohol.

48. The aqueous solution of claim 46, wherein the additional surfactant is a polycarboxylated ethylene oxide condensate of a fatty acid.

49. The aqueous solution of claim 36, further comprising a hydrotrope.

50. The aqueous solution of claim 49, wherein the hydrotrope comprises an alkali metal salt of an intermediate chain length monocarboxylic fatty acid.

Fig.1

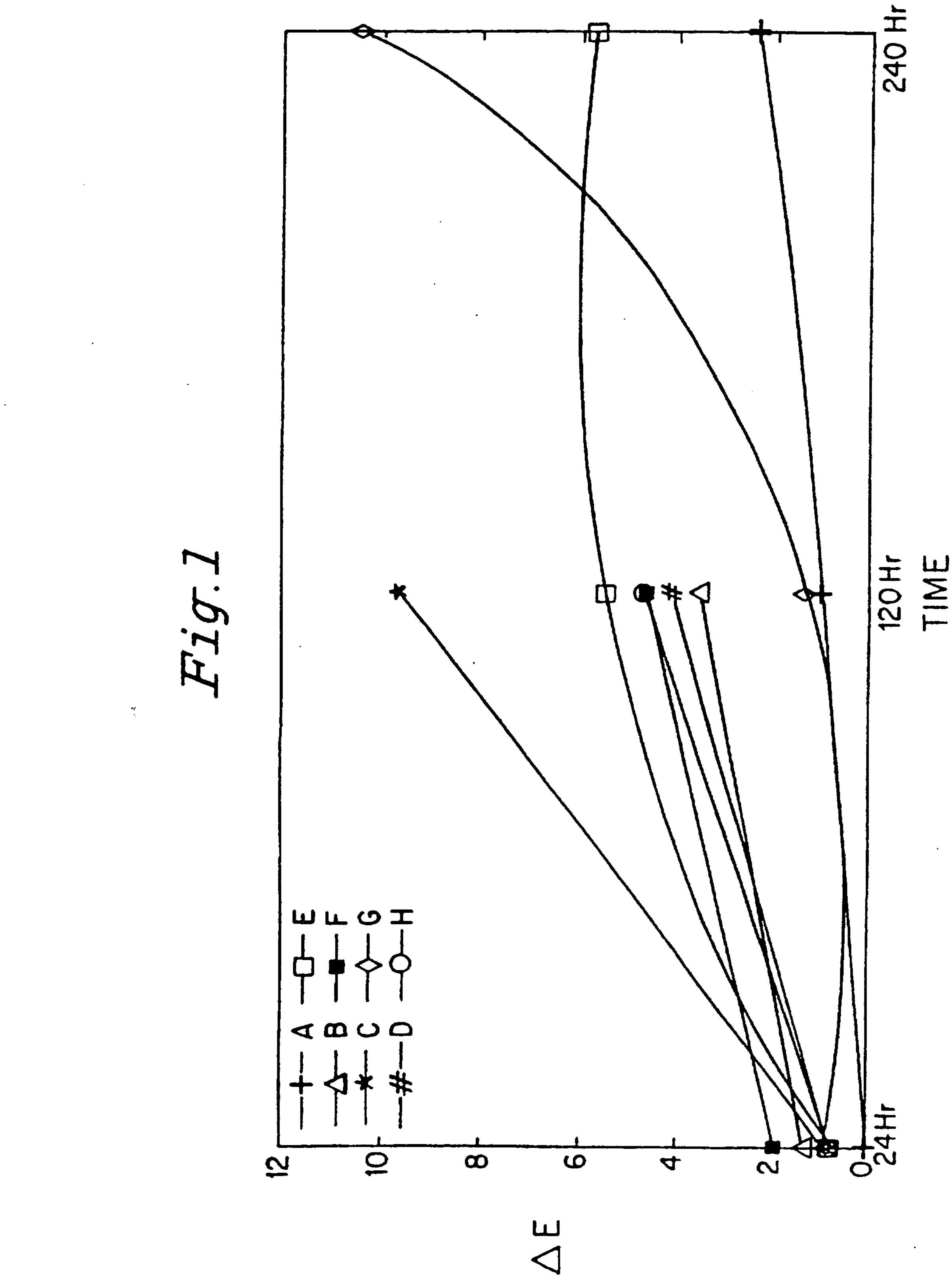
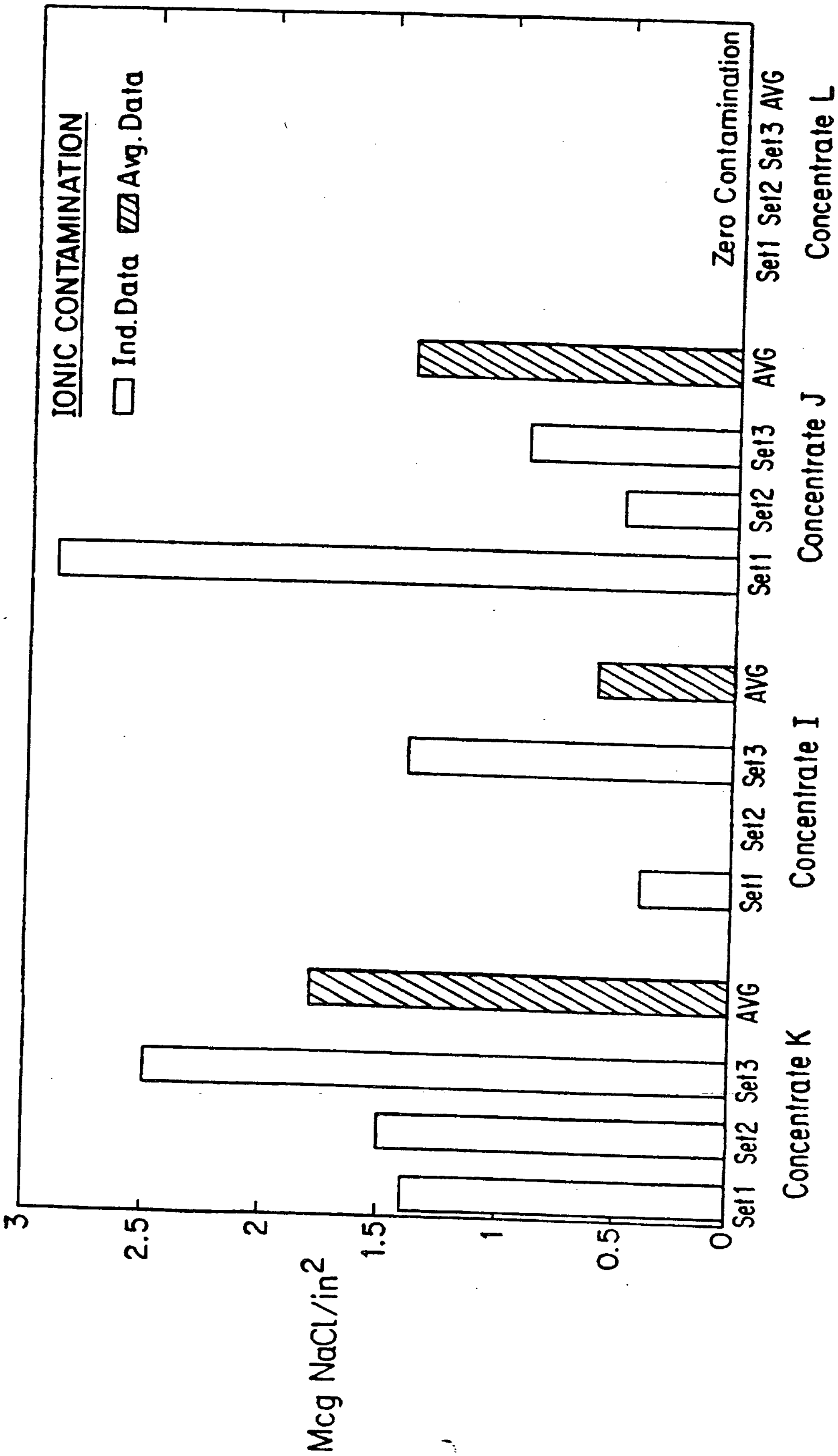


Fig. 3


IONIC CONTAMINATION
Ind. Data
Avg. Data
Mcg NaCl/in2
0
0.5
1
1.5
2
2.5
3
Set1 Set2 Set3 AVG
Concentrate K
Set1 Set2 Set3 AVG
Concentrate I
Set1 Set2 Set3 AVG
Concentrate J
Zero Contamination
Set1 Set2 Set3 AVG
Concentrate L

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/00016

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B08B 3/04, 3/12
US CL :510/175, 254, 255, 245, 420, 421, 252
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/175, 254, 255, 245, 420, 421, 252

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS search terms: pyrrolidone, block copolymer, carbonate, bicarbonate, silicate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,593,504 A (CALA et al) 14 January 1997, col. 12, table 1	1-50
X	US 5,593,339 A (YAM et al) 14 January 1997, col. 4, line 60 - col. 6, line 37	1-50
A	US 4,878,951 A (POCHARD et al) 07 November 1989	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

23 MARCH 1997

Date of mailing of the international search report

07 MAY 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
PAUL LIEBERMAN
Telephone No. (703) 308-0611